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"RADIOLYSIS OF LIQUID CYCLOHEXENE"

by

BRIAN R. WAKEFORD

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES  
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE  
OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

APRIL, 1964





UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "RADIOLYSIS OF LIQUID CYCLOHEXENE" submitted by BRIAN R. WAKEFORD in partial fulfilment of the requirements for the degree of Doctor of Philosophy.





## ABSTRACT

The major products formed in irradiated cyclohexene were hydrogen ( $G_i = 1.28$ ), cyclohexane ( $G_i = 0.95$ ), 2,2'-dicyclohexenyl ( $G_i = 1.94$ ), 3-cyclohexylcyclohexene ( $G_i = 0.60$ ), dicyclohexyl ( $G_i = 0.23$ ), polymer ( $G = 2.3$   $C_6$  units, excluding dimer) and an unidentified dimer ( $G_i = 0.22$ ). The yields of benzene, 1,3- and 1,4-cyclohexadiene were  $<0.05$ ,  $<0.1$  and  $\sim 0.05$  respectively. The major products were not appreciably dependent on dose rate over the dose rate range  $1.3 \times 10^{17} - 2.6 \times 10^{19}$  ev/g hour. The following product yields were obtained for the radiolysis of cyclohexene- $d_{10}$ . Hydrogen ( $G = 0.65$ ), cyclohexane ( $G = 0.66$ ), 2,2'-dicyclohexenyl ( $G = 1.36$ ), 3-cyclohexylcyclohexene ( $G = 0.66$ ), dicyclohexyl ( $G = 0.47$ ) and unidentified dimer ( $G = 0.32$ ).

It appeared from the nature of the products and their distribution, that radicals played an important role in the radiation chemistry of cyclohexene. The most satisfactory explanation for the absence of a dose rate dependence in the cyclohexene product yields appears to be that the cyclohexyl and cyclohexenyl radicals react among themselves, and do not react to an appreciable extent with the substrate in the dose rate region studied.

Both added benzene and added 1,3-cyclohexadiene inhibited all the major products of the cyclohexene system. The latter was the more effective inhibitor. The effect of benzene was apparently due to "sponge type" protection. Energy transfer from cyclohexene to 1,3-cyclohexadiene also occurred. Dimerization of the 1,3-cyclohexadiene, and polymerization were important processes for the solutions of





1,3-cyclohexadiene in cyclohexene.

Added 1,4-cyclohexadiene inhibited all of the cyclohexene type dimeric products, but enhanced the yield of cyclohexane slightly. Both energy transfer from cyclohexene to 1,4-cyclohexadiene and radical reactions with the 1,4-cyclohexadiene appeared to be occurring.



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SECTION I - INTRODUCTION



## SECTION I - INTRODUCTION

### (A) RADIATION CHEMISTRY

#### (a) General

Radiation chemistry is the study of the chemical effects of ionizing radiation on matter. The ionizing radiation may consist of naturally emitted particles ( $\alpha$ - and  $\beta$ -rays), artificially accelerated particles (electrons, protons, deuterons etc.), natural electromagnetic radiation ( $\gamma$ -rays) or artificial electromagnetic radiation (X-rays), (1). In this work the chemical effects of  $\text{Co}^{60}$   $\gamma$ -rays were studied. The disintegration scheme for  $\text{Co}^{60}$  is given in Figure I.1, (2)

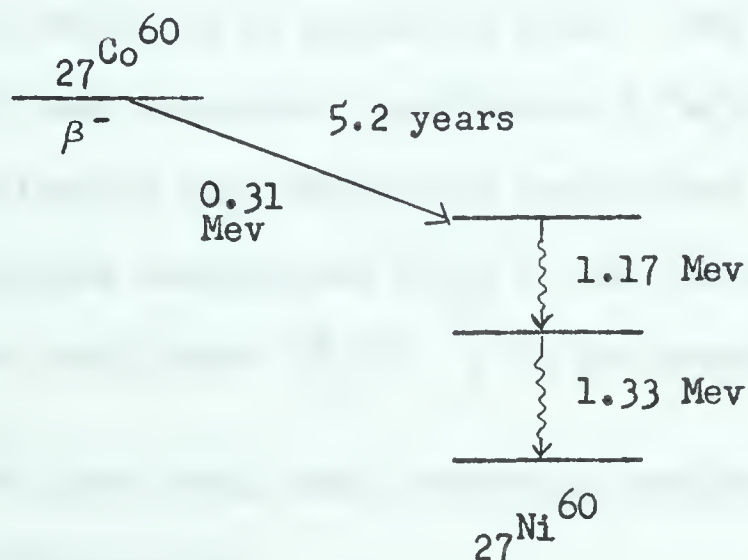


FIGURE I.1

Since 0.31 Mev  $\beta$ -rays can be stopped by 0.3 mm of glass (3), the chemical effects observed resulted from the absorption of the 1.17 and 1.33 Mev  $\gamma$ -rays. The interaction of such  $\gamma$ -rays with matter will be described in the next section.



(b) Interaction of  $\text{Co}^{60}$   $\gamma$ -rays with Matter

Electromagnetic radiation, with photon energies in the region above  $10^3$  ev, might interact with matter by one or more of four processes. These are the photoelectric process, the Compton process, pair production and photodisintegration (4). Photodisintegration is only important for photon energies  $> 20$  Mev. The contribution of each of these processes to the total energy absorbed depends upon the photon energy, and the atomic number of the absorbing material. The Compton process is the only effective type of energy absorption for photons in the 1 Mev energy range, (e.g.  $\text{Co}^{60}$   $\gamma$ -rays), if material of low atomic number is being irradiated. This is demonstrated in Figure I.2, where the relative importance of the different energy absorption processes is shown for water. The solid line gives the true total mass absorption coefficient ( $\mu_a/\rho$ ). The dotted lines show the photoelectric mass absorption coefficient ( $\tau/\rho$ ), the true Compton mass absorption coefficient ( $\sigma_a/\rho$ ), and the pair production mass absorption coefficient ( $\kappa/\rho$ ).  $\rho$  is the density of the absorbing material.

The true total mass absorption coefficient is related to the other coefficients by

$$\mu_a/\rho = \tau/\rho + \sigma_a/\rho + \kappa/\rho$$

It can be seen that, for photon energies in the range of 1 Mev,

$\mu_a/\rho = \sigma_a/\rho$ , (i.e. only the Compton process is operative), since the photoelectric ( $\tau$ ) and pair production ( $\kappa$ ), absorption coefficients are zero.



FIGURE I.2

Absorption of Electromagnetic Radiation by Water

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$\mu_a/\rho$  = True total mass absorption coefficient

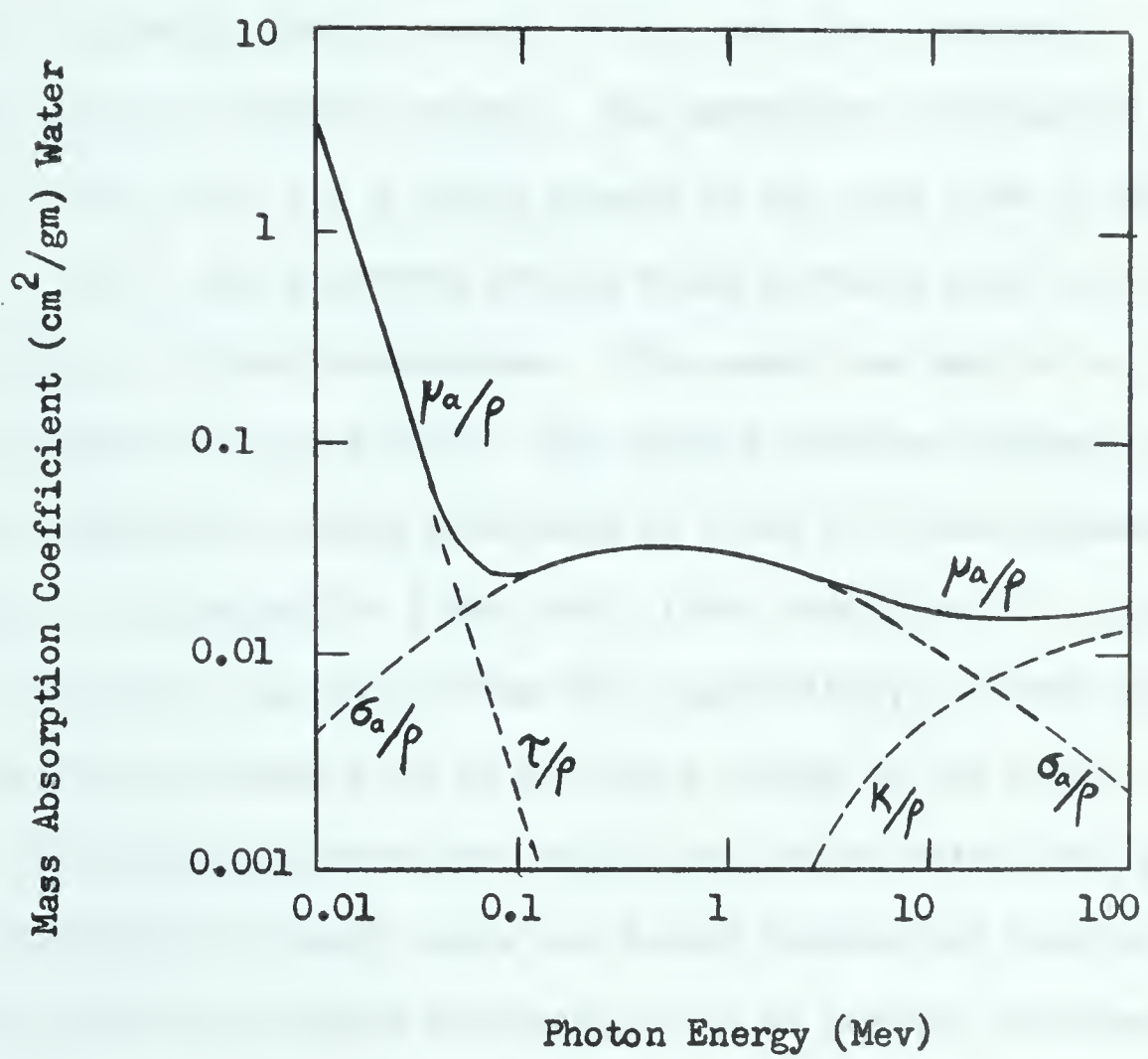
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$\tau/\rho$  = Photoelectric mass absorption coefficient

$\sigma_a/\rho$  = True Compton mass absorption coefficient

$K/\rho$  = Pair production mass absorption coefficient

$$\mu_a/\rho = \tau/\rho + \sigma_a/\rho + K/\rho$$





(c) The Compton Absorption Process

The Compton absorption coefficient per atom is proportional to the atomic number,  $Z$ . Thus the relative amount of absorption by different compounds is proportional to the electron density of the compounds. In this process, if the incident photon interacts with an electron, it imparts kinetic energy to it, and also produces a scattered photon of reduced energy. The absorption coefficient for  $\gamma$ -rays is such that, for a liquid sample of the size used in this study (1 - 2 ml), the scattered photon would normally pass out of the system, without further interaction. (The mean free path of a 1 Mev photon in water is 33.3 cm (5)). The ejected electron (primary electron), which may possess any energy from zero to 1 Mev (2), then interacts with the system. The ranges for 1 Mev and 0.1 Mev electrons, in a hydrocarbon liquid, are about 4 mm and 0.15 mm (5), respectively, so that most primary electrons formed give up all their energy to the system. A 1 Mev electron is involved in more than 10,000 collisions before being stopped (2). Along the collision "track" there are formed ionized and excited molecules. The average distance between ionizations due to primary electrons of 450 kev energy is about 4,5000  $\text{\AA}$  (6). Some of the electrons ejected from the molecules (secondary electrons), have enough energy to cause further ionization as well as excitation. These ionizations usually occur within a few Angstrom units ( $\sim 10 - 15 \text{\AA}$ ) (7) of the site of formation of the secondary electron involved. The group of ion pairs so formed, constitutes a "spur" (8).





The ionized and excited intermediates, formed during the initial deposition of energy, undergo, or lead to, chemical reactions. The chemical effects observed are caused by the passage of the energized electrons, so that the reactive intermediates are not, therefore, characteristic of  $\gamma$ -rays only, since other forms of ionizing radiation also give rise to fast electrons. The spatial distribution of these intermediates does depend on the type of radiation used, however, and this can cause significant differences in the product distribution in a radiolytic system if incident radiations of widely different types are used (effect of linear energy transfer, L.E.T.) (9) (10) (11).

The process of transferring the energy from an interacting  $\gamma$ -ray to the radiolytic system and forming the reacting intermediates, as described above, takes  $10^{-15}$  sec (12). Thus this process is complete before any chemical change can take place. The elementary processes that are undergone by the reactive intermediates are not well understood. The types of processes considered possible, will be reviewed in the following sections. The initial fates of the ionic intermediates and electrons will be considered first.

(d) Fates of the Ionic Intermediates and Electrons - Considerations

We are concerned with the competition between (1) unimolecular rearrangement or dissociation of the ions (2) bimolecular ion-molecule reactions, and (3) electron capture by a positive ion (leading to reactions typical of excited molecules).

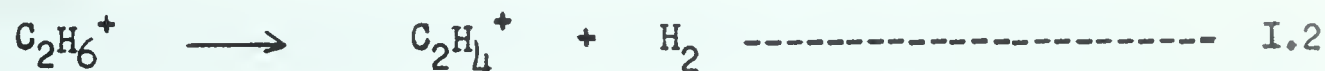


No direct information is available about any of these processes, as applied to condensed hydrocarbon systems. However, unimolecular rearrangements and dissociations, and ion-molecule reactions have been studied at low pressure (up to  $10^{-2}$  mm for secondary processes), by mass spectrometry for many years (13) (14). Examples of the types of reaction that have been observed are given below.

(1) Unimolecular Rearrangement and Dissociation of Ions

Mass spectral data gives evidence for such processes (15). For example the  $C_2H_5^+$  ions, in the mass spectra of neopentane, cyclohexene and cyclohexane, must result from unimolecular rearrangement and dissociation processes, since they are observable at pressures that are so low (i.e.  $\sim 10^{-6}$  mm Hg), that collisional processes cannot take place during the residence time of the ions in the mass spectrometer.

Examples of unimolecular dissociations are (16)



It can be seen that both radical and molecular species may be formed.

(2) Ion-Molecule Reactions (13)

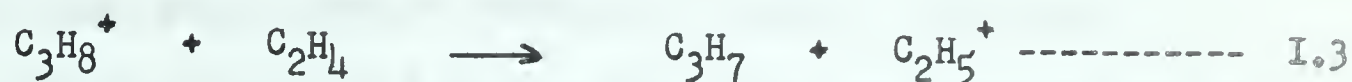
Ion-molecule reactions for hydrocarbons may be summarized in five categories, as follows





(i) Proton Transfer

An example of such a reaction is



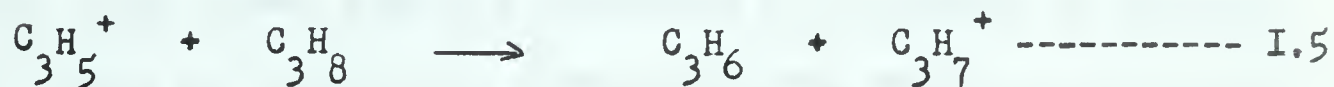
(ii) Hydrogen Atom Transfer

For example

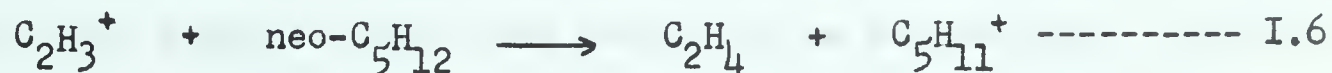


(iii) Hydride Ion Transfer (17)

An example of such a reaction is



In many of the hydride ion transfer reactions reported, one of the products was a neutral molecule. In some cases an exothermic dissociation reaction for this neutral molecule was available. For example the  $\text{C}_2\text{H}_4$  species formed in the reaction,



may dissociate to give hydrogen and acetylene

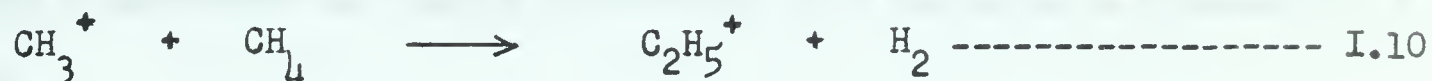
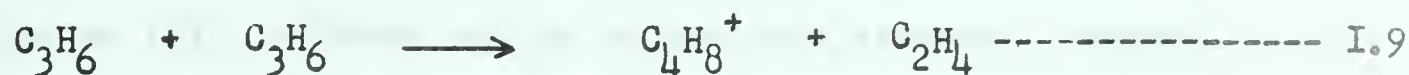
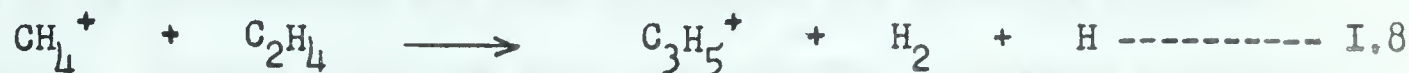






(iv) Condensation Type Reactions

Such reactions are characterized by more complex molecular rearrangement than simple atom or atomic-ion transfer. C-C bond formation is a major feature. Reactions that have been reported include



(v) Negative Ion Reactions

Some such reactions are reported, but none involving pure hydrocarbons. Both theory (18) and experiment (19) indicate an electron affinity of  $\sim$ zero for alkanes and alkenes, but the degree of interaction between a free thermalized electron and surrounding neutral molecules in a condensed hydrocarbon system has not been determined.

(3) Electron Thermalization and Capture by a Positive Ion

The positive and negative charges produced by the passage of ionizing radiation through matter must eventually be neutralized. The life times of the charged species are not known. Two calculations have been made to determine the probable behaviour of the electrons prior to capture by a positive ion (20) (21). Both calculations applied to pure water. Samuel and Magee (20) calculated that an electron was recaptured by its parent ion in  $\leq 10^{-13}$  sec. The Platzman calculation (21) leads to the conclusion that the



electron escapes from the field of the parent ion, due to interaction with a polar solvent.

There is now experimental evidence that at least some of the electrons escape the parent ion and are trapped in the bulk liquid. A half life of 16 microseconds has been determined for solvated electrons in water (22). Trapped electrons have been observed in several irradiated organic glasses (23), although not in alkanes and alkenes. However, conductance measurements in liquid cyclohexane have indicated a  $G(\text{escaped } e^-) = 0.2$  (24).

(e) Fates of Ionic Intermediates and Electrons - Conclusions

The gas phase ion-molecule reactions that have been observed in the mass spectrometer apparently occurred at every collision. An activation energy of  $\sim$ zero must be assumed for these reactions in order to obtain reasonable values for collision cross-sections (13). This conclusion is borne out by the lack of temperature dependence for these reactions (25). Thus in a condensed hydrocarbon system, the time required for an ion to take part in a bi-molecular reaction involving mass transfer (i.e. H-atom, proton or hydride ion transfer) may be as short as  $\sim 10^{-14}$  sec (the period of vibration for a C-H bond (26)), so even the most rapid electron-ion recombination suggested does not preclude the possibility of an ion-molecule reaction. Systems have been studied for which it is difficult to ascribe the formation of some or all of the radiolytic products to any mechanism other than one involving ion-molecule reactions (27) (28) (29). These will be described more fully later .





(f) Fates of Excited Molecules

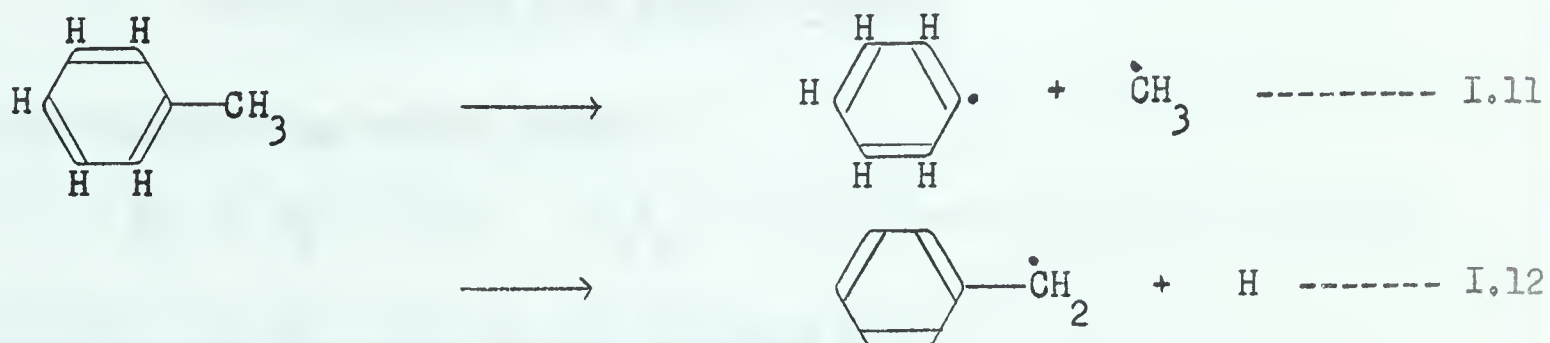
Excited molecules may be formed in the track during the initial excitation, or may result from ion-electron recombination. The excited species formed by ion neutralization may be chemically different from excited substrate molecules if the ion is a product of an ion-molecule reaction. An excited molecule,  $M^*$ , may be deactivated by collision or by photon emission or it may undergo chemical reaction. The types of reaction that could occur in a pure liquid include,

- (1)  $M^* \longrightarrow \text{Radicals}$
- (2)  $M^* \longrightarrow \text{Molecular Dissociation Products}$
- (3)  $M^* \longrightarrow \text{Isomerization Products}$
- (4)  $M^* + M \xrightarrow{(M^*)} \text{Products}$

These will be discussed below.

(1) Dissociation into Radicals

Homolytic bond cleavage yields two free radicals. Both C-C and C-H bond cleavage are commonly observed. e.g.

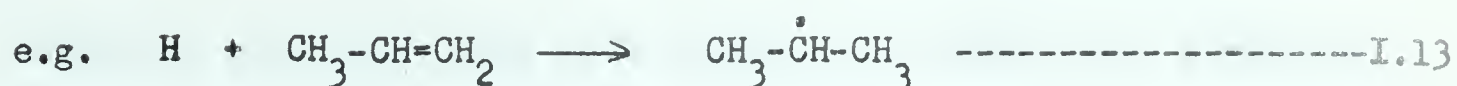


Free radicals have been detected in hydrocarbons under radiolytic conditions (30) (31) (32). Studies of free radical reactions, mainly in the gas phase, indicate that the radicals can react by the following processes (33).

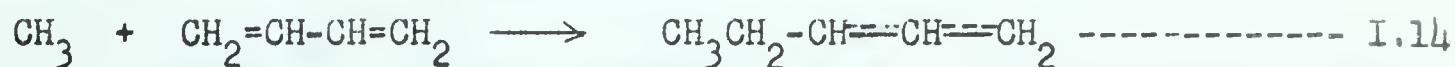




(i) Addition to an Olefin (Giving Another Free Radical)

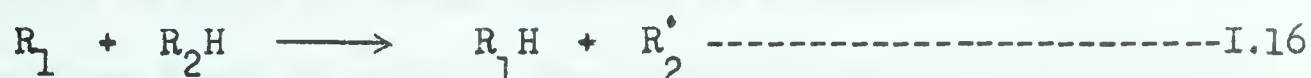


Addition of a radical to a conjugated double bond system occurs more readily than to a mono-olefinic molecule (34) (35), because the resultant radical is resonance stabilized. For example



Typical activation energies are  $\sim 7$  and  $\sim 2.5$  kcal/mole for the addition of methyl radicals to mono-olefins and conjugated di-olefins respectively. H-atom addition to a mono-olefin has an activation energy of  $\sim 5$  kcal/mole (36).

(ii) Metathetical Reactions (Involving H-atom Transfer)



Such reactions have an activation energy of  $\sim 8$  kcal/mole.

(iii) Reaction with Another Radical

Two radicals may either combine



or disproportionate (involving H-atom transfer) e.g.



These processes have an activation energy of  $\sim 0$  kcal/mole.

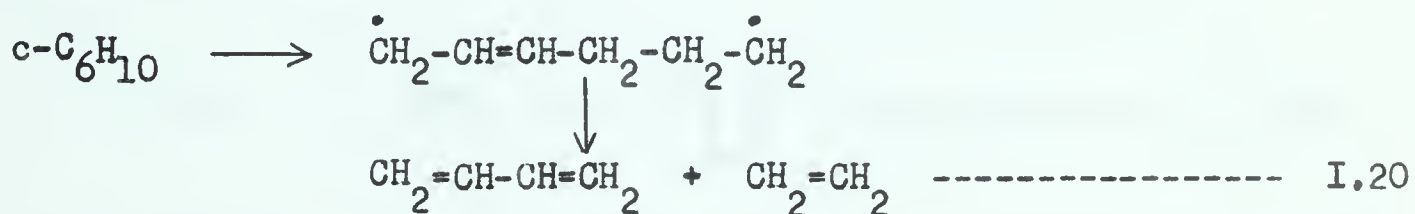


## (2) Dissociation into Molecular Products

Molecular elimination has been suggested to explain the formation of hydrogen that cannot be inhibited by the addition of low concentrations of radical scavengers (< 2% scavenger). In the radiolysis of cyclohexane, for example, the following one step reaction has been proposed (37) to account for the formation of "unscavengeable" hydrogen



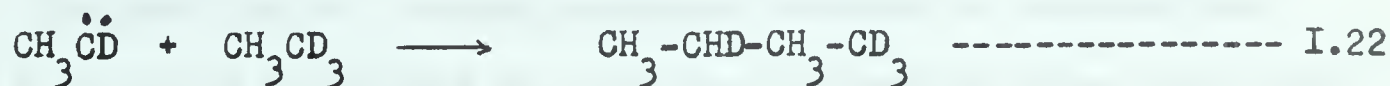
Some fragmentation products in the radiolysis of cyclohexene have been explained (38) by the reaction,



A reaction in which molecular hydrogen is eliminated from one carbon atom has been shown to occur in the vacuum ultra-violet photolysis of ethane (39)



The ethylidene radical so formed apparently inserts into a C-H bond to give n-butane as shown below

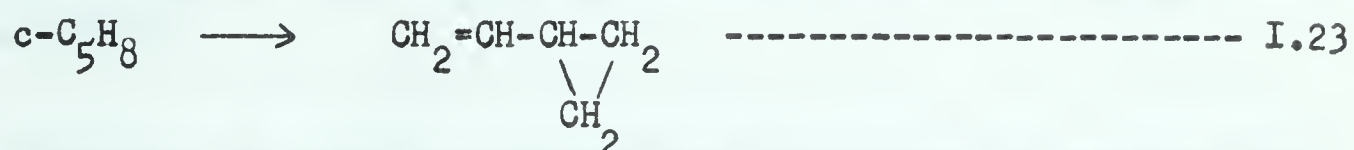






### (3) Isomerization

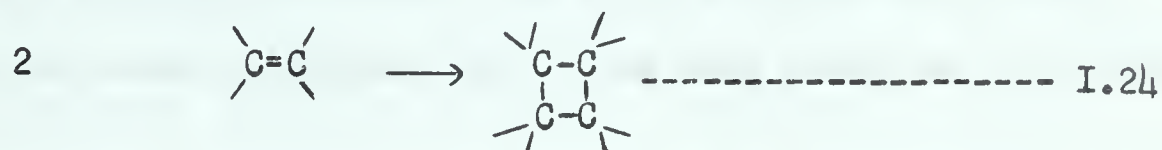
Intra-molecular rearrangement may occur. For example, in the mercury photosensitized decomposition of cyclopentene (40), vinyl cyclopropane formation was reported, i.e.



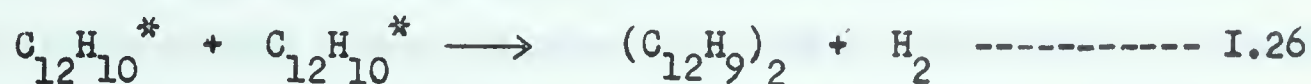
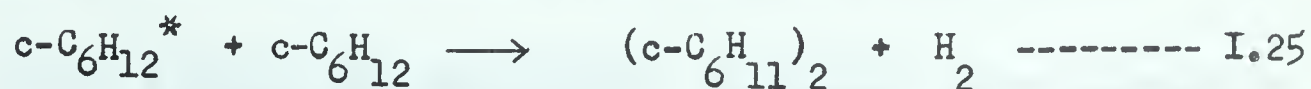
### (4) Bimolecular Reactions

Photo addition has been observed for olefins (41) (42) (43).

The reaction has the general form,



Bimolecular reactions, involving excited molecules in radiolytic systems, have been suggested (44) e.g.,



### (g) Additional Processes for Two Component Solutions

The addition of a second component (solute) to a radiolytic system can inhibit or promote the formation of products from the initial component (solvent). These effects may result from energy or charge transfer, giving solvent protection (45) (46) or sensitization (47), or





the solute may inhibit the formation of certain products by scavenging their free radical precursors or electrons. Schuler (48), has given a detailed account of scavengers and scavenging mechanisms. The processes that he describes also apply to olefins, which can act as radical scavengers, with ranging degrees of efficiency, depending on the system (35) (49) (50).

Transfer of energy or charge from the solvent to a solute that has lower lying excited or ionized states can result in protecting the solvent from decomposition (45). The effectiveness of inhibition, by a low concentration of solute, will depend on the rapidity of solvent decomposition. Four modes of energy (including charge) migration have been proposed for crystalline solids, and it is believed that these processes may also occur in liquids (51). The four modes are as follows.

(i) Exciton:- The excitation energy may be transferred in the form of an exciton. In this process the electronic excitation is transmitted through the molecules from neighbour to neighbour.

(ii) Positive Hole Migration:- The energy can be carried by excited electrons and their positive holes moving independently through the lattice.

(iii) Virtual Photon:- This is the transfer of an energy packet over distances of several molecular diameters without the existence of a photon as an intermediate. The donor and acceptor molecules must have overlapping emission and absorption spectra.



(iv) Photon Emission:- The initial absorption can be followed by photon emission, and this emitted radiation may be reabsorbed in a solute molecule.

The rapidity of energy transfer by process (i) and (ii) above may be influenced by the "structure" of the liquid. For example the difference in melting point between benzene ( $5.5^{\circ}\text{C}$ ), and cyclohexene ( $-103.7^{\circ}\text{C}$ ), indicates a disorganized structure in cyclohexene. Thus energy transfer by exciton or positive hole migration may occur less readily in cyclohexene than in benzene.

Other processes for protecting solute molecules from decomposition have been discussed (45). These include quenching, in which the solute molecules promote distribution of the initially localized energy among vibrational-rotational degrees of freedom of neighbouring solvent molecules, and negative ion formation, in which the solute molecules trap electrons before they can recombine with the positive ions.

#### (h) Some Effects of Phase in Radiation Chemistry

A great deal of the fundamental information, used to interpret experimental observations in liquid phase radiation chemistry, was obtained from kinetic studies that were carried out in the gas phase. For example the direct observation of ion-molecule reactions has only been possible under vapour phase conditions in a mass-spectrometer and much of the kinetic data for free radical reactions were obtained from the pyrolytic and photolytic studies of gas phase systems. Although the information thus obtained is frequently extrapolated to liquid phase radiolytic systems, it







is borne in mind that, in many respects, reactions in the gas and liquid phase are not the same. The rate of diffusion of molecules in a liquid material is much slower than it would be if the material was in the vapour phase, due to the close packing of molecules in a liquid. An individual molecule may be considered to be in a "cage" (52) of surrounding molecules. A reactive species formed during radiolysis, is also in such a cage.

An "encounter" between two species, A and B, is said to begin when B diffuses into the wall of the cage surrounding A, or vice versa, and the encounter ends when either A or B diffuses away. Many collisions between A and B may occur during one encounter. The cage effect is particularly important in radiation chemistry due to the inhomogeneity in the distribution of the reactive intermediates formed during primary activation. Thus excited species, formed adjacent to each other in the primary excitation track, have a much higher probability of reacting with each other in the liquid phase than they would have in the gas phase. On the other hand, a radical that is isolated (as it may be for example if it were formed by H-atom addition to an olefin in the bulk solution), may have a high probability of reacting with an adjacent substrate molecule in the "cage", even though such a reaction has an appreciable activation energy (e.g. a metathetical reaction for which only 1 in  $\sim 10^5$  collisions may be reactive).

Unimolecular processes that are important in the vapour phase may be prevented from occurring in the liquid, due to intervention of adjacent molecules. Also the mechanism of inhibition for a given system may be



phase dependent. Free radical scavengers can be expected to be less effective in a liquid system due to the track effect, while some of the rapid energy transfer processes, described earlier, can be effective only in a condensed medium.

The effects of phase on the radiolysis of cyclohexane (53) (54) and n-hexane (55) have been studied. One observation was that the yields of products arising from C-C bond cleavage were much lower in the liquid phase than they were in the gas phase. This may be due to the cage effect or to the formation of different energy states in the liquid phase.

The yields of products arising from C-H bond cleavage were not so drastically reduced by condensation of the medium. This may be due to the more facile diffusion of the small H-atoms from a cage.





(B) LIQUID OLEFINIC HYDROCARBON RADIOLYSES

(a) General

Free radicals, ions and excited molecules have been suggested as intermediates participating in the final reaction steps that lead to the measured products of liquid hydrocarbon radiolyses. In many of these studies there was no experimental distinction between the types of mechanism, so that alternative modes of product formation could not be excluded. Some of the less ambiguous results have been obtained from the irradiation of various types of olefin.

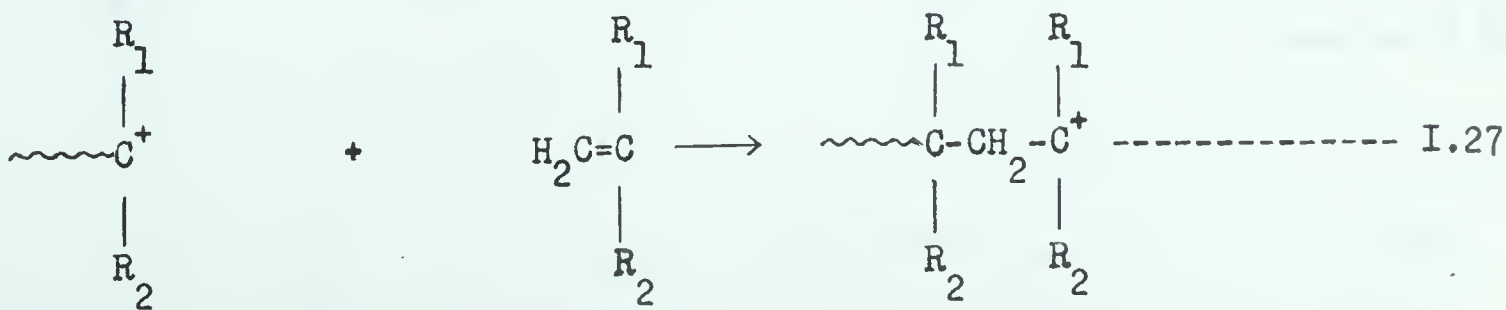
Examples of mechanisms that have been suggested to account for the formation of various products in irradiated liquid olefins, will be outlined in the following sections.

(b) Long Chain Polymerization

(1) Ionic Mechanism

Cationic chain polymerization has been suggested as the major process in the radiolysis of several vinylidene type olefinic hydrocarbons (29) (56) (57) (58) (59).

The chain propagation process may be generalized as



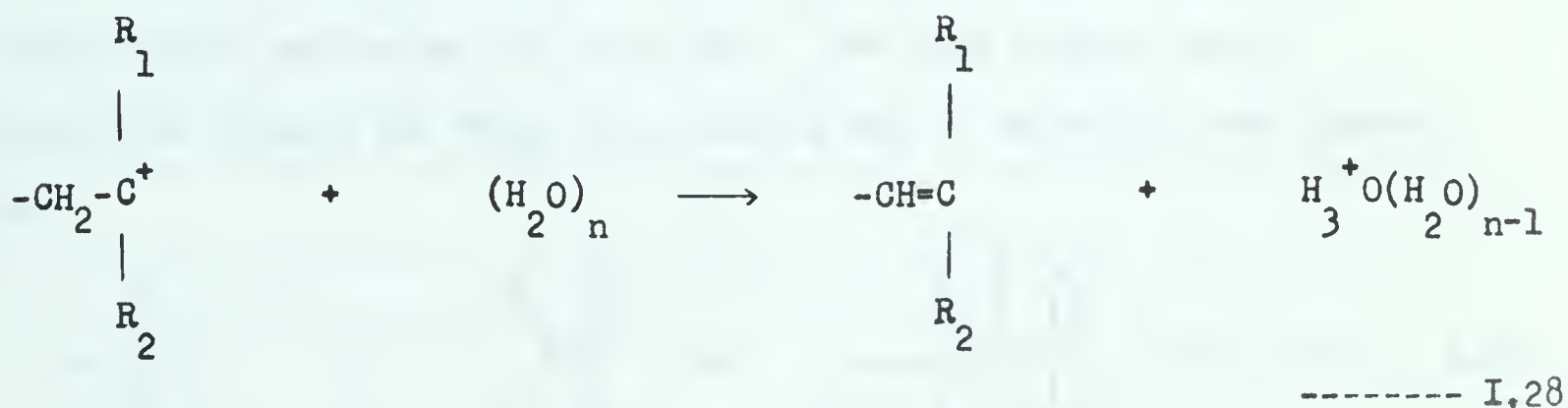




The  $\gamma$ -ray induced polymerization of isobutene at  $-78^{\circ}\text{C}$  (29) has been clearly shown to proceed by an ionic mechanism. Uncharged radicals, formed in the isobutene at  $-78^{\circ}\text{C}$ , did not induce polymerization, whereas gamma irradiation of the pure isobutene, at this temperature, did induce polymerization with a  $G(-\text{C}_4\text{H}_8) = \sim 300$ . Addition of radical scavengers did not affect the reaction.

Irradiation of  $\beta$ -pinene (57) (58) and  $\alpha$ -methyl styrene (57) (59) also induced chain polymerization. These two monomers were irradiated in the presence of water and also after careful drying. In the presence of water ( $G - \alpha$ -methyl styrene) = 10 and  $G(-\beta$ -pinene) =  $\sim 6$ , whereas drying gave values for monomer consumption as high as  $G(-\alpha$ -methyl styrene) = 10,000 and  $G(-\beta$ -pinene) =  $> 2000$ .

The marked reduction in monomer consumption by water was suggested as unequivocal evidence for an ionic mechanism. Chain termination by proton removal from a cationic centre, as shown in the reaction I.28, is likely to be exothermic, due to the heat of solvation of the hydronium ion.





The alternative free radical termination steps, given by the reactions



and

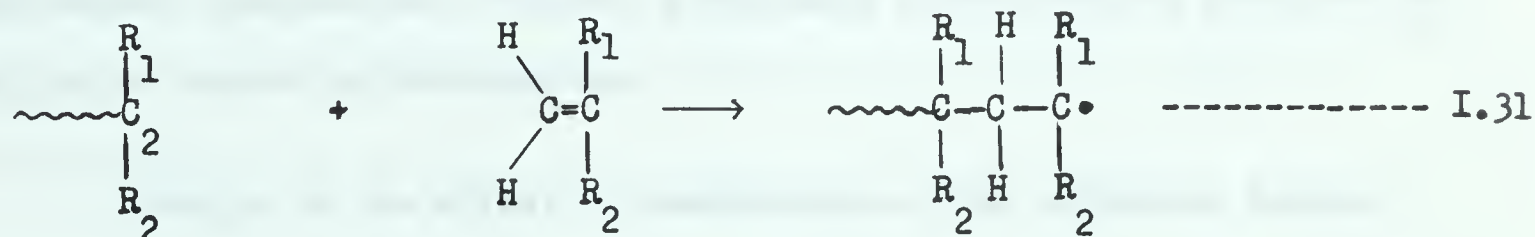


are endothermic and also give rise to further chain initiators.

The above three compounds belong to a class of materials noted for undergoing polymerization by means of a cationic mechanism (60). Thus if any of the electrons, produced in the initial radiolytic act, escape from their parent ions, rapid cationic polymerization might be expected. A value of  $G(\text{free ions}) = 0.2$  was reported for saturated hydrocarbon systems (24). These ions could, therefore, account for the polymerization.

## (2) Free Radical Mechanism

Many radiation induced polymerizations appear to proceed by a free radical mechanism (61) (62) (63). The free radical chain propagation process for vinyl type olefins may be written in the general form



Styrene, methyl methacrylate and tetraethylene glycol methacrylate are monomers for which there is good evidence in favour of a free radical

Let  $x$  and  $y$  be any two numbers. Then  $x + y$  is a number.

$$(x + y) + z = x + (y + z) \quad \text{for any } x, y, z.$$

$$(xy)z = x(yz) \quad \text{for any } x, y, z.$$

Let  $x$  be any number. Then  $x + 0 = x$  and  $x \cdot 1 = x$ .

Let  $x$  be any number. Then  $x + (-x) = 0$  and  $x \cdot (1/x) = 1$ .

Let  $x$  and  $y$  be any two numbers. Then  $x + y = y + x$  and  $xy = yx$ .

Let  $x$  and  $y$  be any two numbers. Then  $x(y + z) = xy + xz$  and  $(x + y)z = xz + yz$ .

Let  $x$  and  $y$  be any two numbers. Then  $x(yz) = (xy)z$  and  $(x + y)z = xz + yz$ .

### THEOREM 1.1

Let  $x$  and  $y$  be any two numbers. Then  $x + y = y + x$  and  $xy = yx$ .

Let  $x$  and  $y$  be any two numbers. Then  $x(y + z) = xy + xz$  and  $(x + y)z = xz + yz$ .

Let  $x$  and  $y$  be any two numbers. Then  $x(yz) = (xy)z$  and  $(x + y)z = xz + yz$ .

$$(x + y) + z = x + (y + z) \quad \text{for any } x, y, z.$$

Let  $x$  and  $y$  be any two numbers. Then  $x + y = y + x$  and  $xy = yx$ .

Let  $x$  and  $y$  be any two numbers. Then  $x(y + z) = xy + xz$  and  $(x + y)z = xz + yz$ .



polymerization mechanism. This evidence has been built up on the basis of inhibition, copolymerization, and temperature studies, and also from comparisons between radiation induced polymerizations and polymerizations initiated in other ways.

For example, the polymerizations of styrene, methyl methacrylate and tetraethyleneglycol dimethacrylate were inhibited by the addition of a low concentration ( $< 1\%$ ) of benzoquinone and also by the presence of oxygen (62) (64). Since both benzoquinone and oxygen are known to react with free radicals and apparently do not greatly affect ionic processes, this was taken as evidence in favour of a free radical mechanism.

Supporting evidence in favour of a free radical mechanism for the radiation induced polymerizations of styrene and methyl methacrylate was obtained from a study of the copolymerization of these two compounds. The radiation induced copolymerization of an equimolar binary solution of styrene and methyl methacrylate yielded a copolymer with a methyl methacrylate content of  $\sim 50\%$ . Similar copolymerization studies have been carried out using other means of chain initiation (65). The methyl methacrylate content of the copolymer, formed from a similar equimolar solution was, 49%, 1% and 99% for free radical, cationic and anionic chain initiation, respectively, thereby indicating a free radical path for the radiation induced polymerization.

Studies of the effect of temperature on the radiation induced polymerization of styrene, methyl methacrylate and tetraethylene glycol dimethacrylate have added weight to the conclusion that these polymerizations follow a free radical path. Overall activation energies



of 7.15 and 4.9 kcal/mole were reported for the  $\gamma$ -ray induced polymerizations of styrene and methyl methacrylate respectively. These values are of the order to be expected for free radical polymerization. Ionic polymerizations have overall activation energies of  $\sim$  zero (61). A positive temperature coefficient was also reported for the radiation induced polymerization of tetraethyleneglycol dimethacrylate (64).

(c) Dimerization and Associated Processes

The 1-hexene system will be used to demonstrate possible ionic and free radical processes for dimerization. This is because it is possible to compare the 1-hexene radiolysis results (28) with the radical induced dimerization a similar compound, 1-octene (66). Furthermore, many of the factors that apply to the 1-hexene system, and influence the choice of mechanism to describe the radiolysis, apply also to the subject of the present study, cyclohexene.

The radiolyses of several straight chain, terminal olefins have been studied. These include the radiolyses of 1-hexadecene (67), 1-octene (28), and 1-butene (68) as well as 1-hexene. It was concluded in all these cases that an ionic mechanism predominated. The conclusions are based mainly on the failure of a free radical mechanism to account for either the nature of the dimeric products or the lack of substrate isomerization.

Possible ionic and free radical mechanisms will be outlined below for the 1-hexene system. Following these, the mechanism for the radiolytic dimerization of 1-hexene, will be discussed.

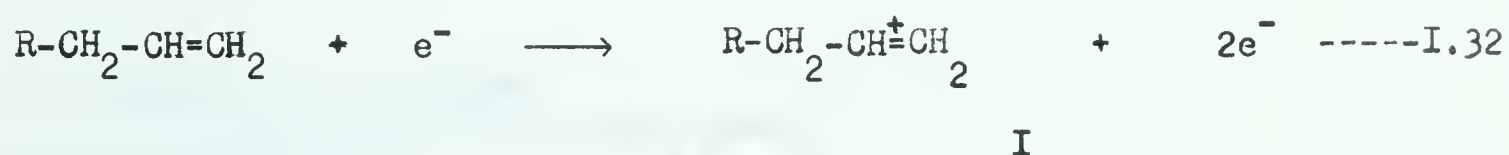




# (1) Ionic Mechanism

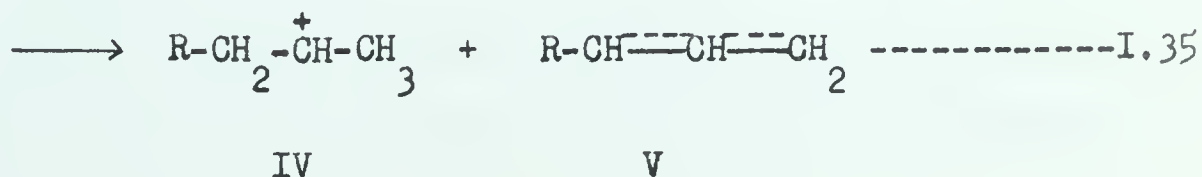
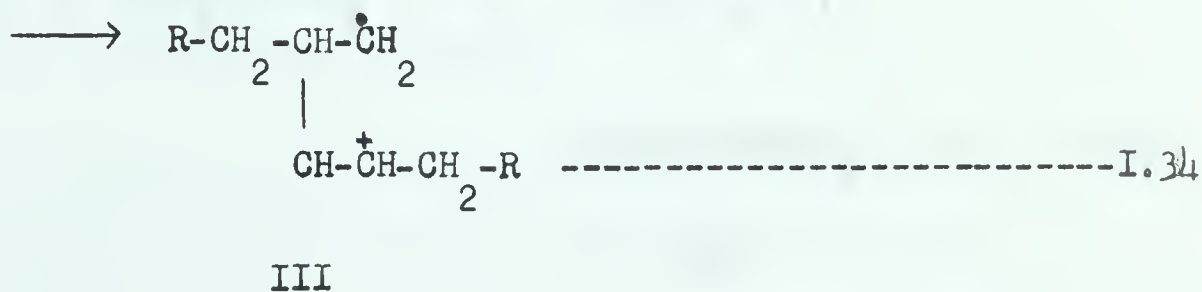
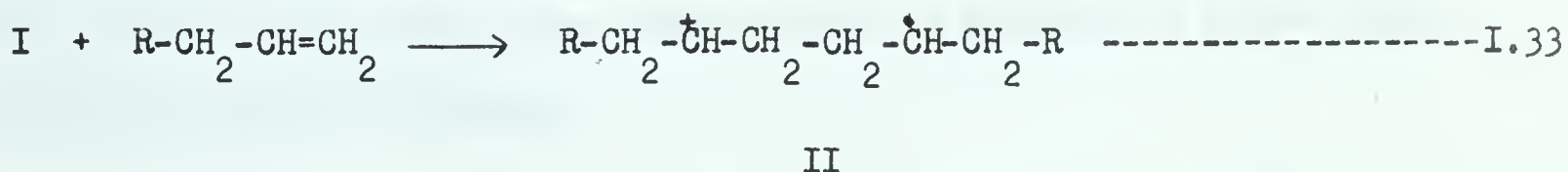
For the sake of brevity the ionic mechanism given will not be exhaustive. Neutralization of an ion may take place at any stage of the mechanism, giving rise to an excited molecule or excited radical, either of which may react in a number of ways. Many such reactions, which are theoretically possible, will not be included in the following scheme.

The initial ionization may be represented by



where R is  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$

The ion formed, I, may combine with a neutral 1-hexene molecule, or, as suggested by Collinson et al (67), transfer a proton to a substrate molecule. These reactions are as follows

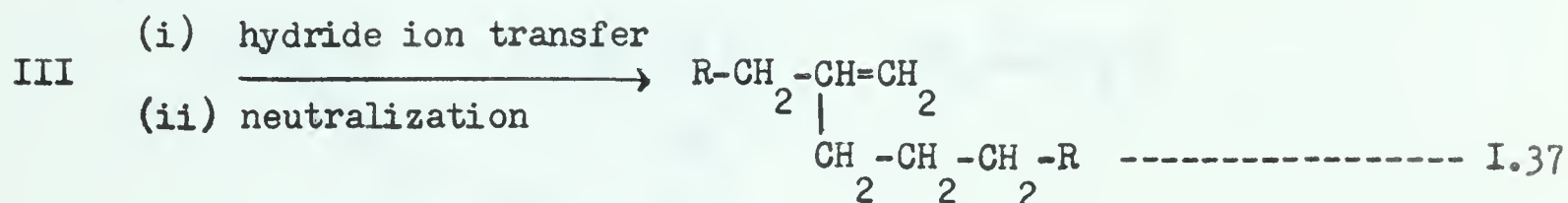
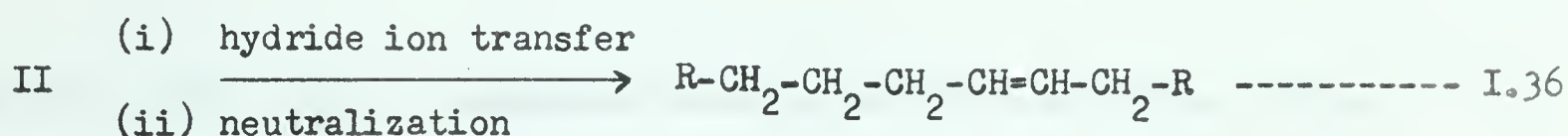






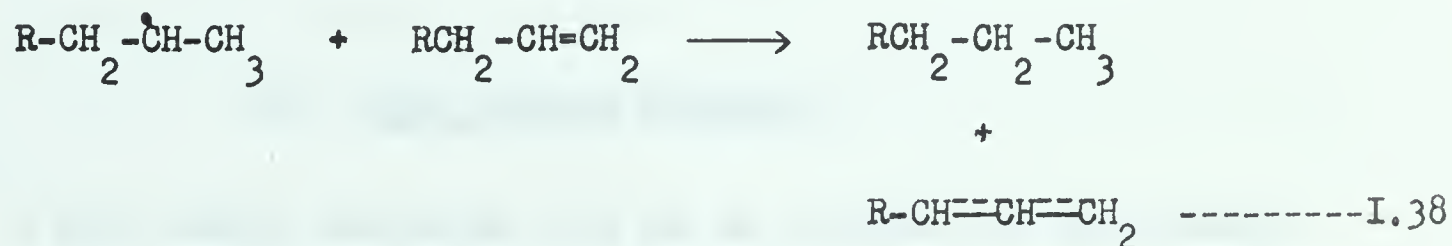
The structures II and III have been suggested as the most probable for the result of a union between ion I and 1-hexene (28).

If the species II and III undergo intramolecular hydride ion transfer, followed by neutralization, then mono-olefinic dimers will be formed as shown below



The ion IV, formed in reaction I.4, may be neutralized or may induce chain polymerization.

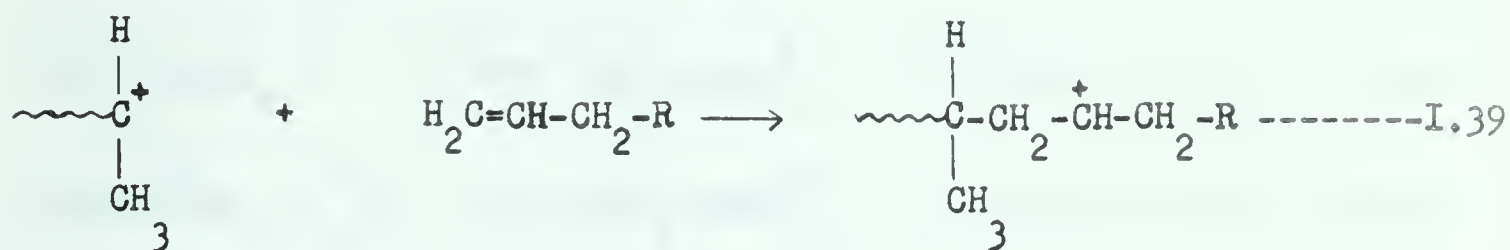
Neutralization of IV will give a hexyl radical that can either react with another radical (see next section) or abstract an H-atom from a substrate molecule as shown by



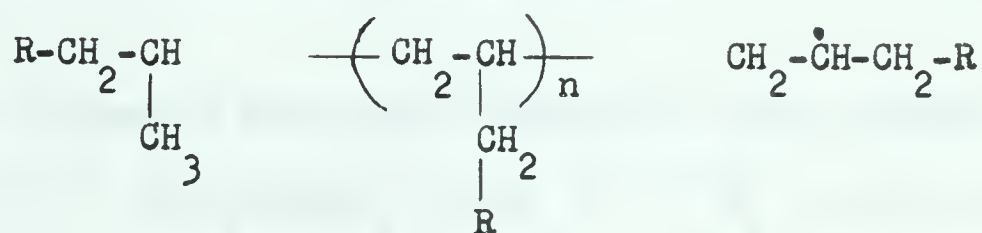
VI



If ion IV induces ionic chain polymerization, the propagation process will be



The ionic chain will be terminated when neutralization occurs, giving rise to a radical of the type



where  $n = 0, 1, 2 \dots\dots$

These radicals, and those formed in steps I.35 and I.38, will undergo the types of reaction that will be outlined in the next section.

If  $n = 0$  for the above radical, then a dimer can be formed from it that will be either saturated or mon-olefinic.

## (2) Free Radical Mechanism

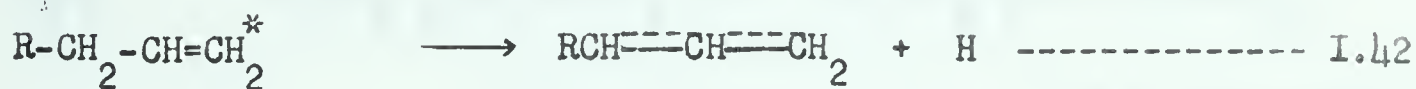
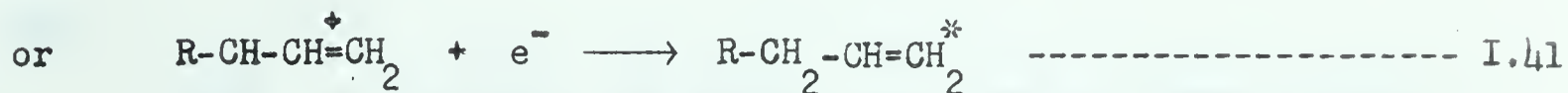
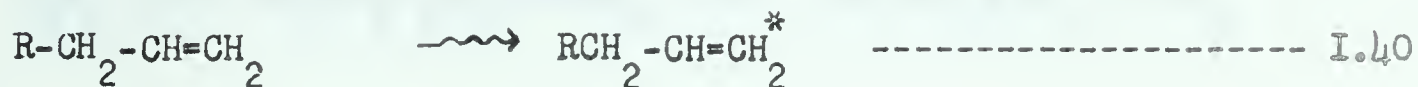
A free radical mechanism will now be outlined for the 1-hexene dimerization. An assumption is made that the observed products would arise from C-H cleavage at the 3-position only. This mode of cleavage, giving rise to allylic type radicals, is energetically favoured (69) and is observed to predominate in terminal olefinic systems, where the reaction is initiated by





free radicals (66).

The initial reaction steps will be



VI

where \* indicates an excited molecule.

The H-atom can react with substrate to give further radicals



VII

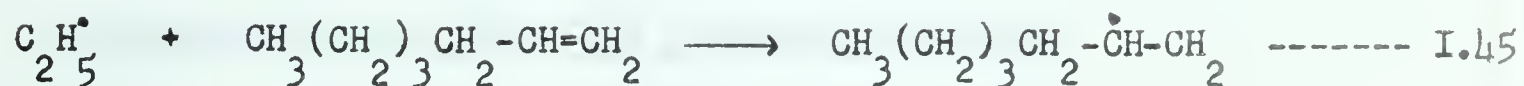
Radical VII is considered to be mostly the sec-hexyl radical, since this species is  $\sim 5$  kcal more stable than the n-hexyl radical, (70). The hexyl and hexenyl radicals formed in steps I.11, I.12 and I.13 may react by any one of three types of process. A radical may (i) react with another radical, (ii) abstract or H-atom from 1-hexene in a metathetical reaction or (iii) add to 1-hexene.

James and Steacie (71) (72) have reported the values of

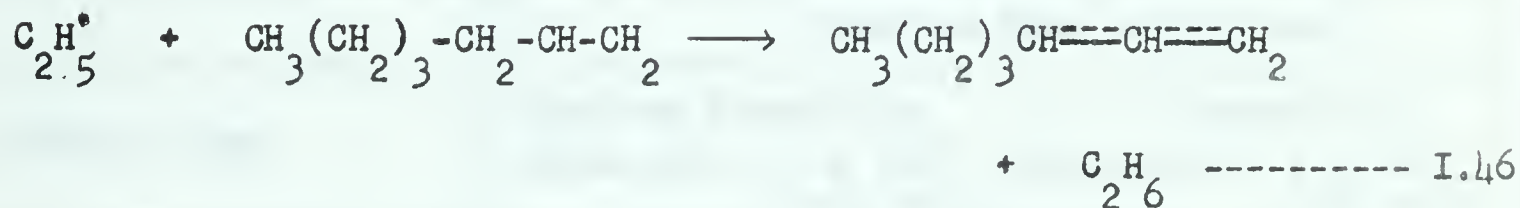
$k = 3.2 \times 10^{-13} \exp(-8000 \pm 700)/RT \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  and  $k = 9.0 \times 10^{-13} \exp(-9300 \pm 700)/RT \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ , for the addition and metathetical reactions, respectively, of ethyl radicals with 1-heptene, in the gas phase.



i.e. for reactions



and



respectively.

If these rate constant values are applied to the reactions of hexyl and hexenyl radicals with 1-hexene\*, and a value of  $k = 10^{10} \text{ l mole}^{-1} \text{ sec}^{-1}$  is assumed for the diffusion controlled, radical-radical reactions (73), then crude estimates of relative rates for the reaction processes (i) (ii) and (iii) above, can be calculated. The values for the rates of these reaction types are compared in Table I.1. The values are given as order of magnitude, and were calculated for two different dose rates, assuming  $G(\text{radicals}) = 10$ .

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\* It is realized that the resonance stabilized hexenyl radicals will have a longer average life-time than the hexyl radicals, and so are relatively more likely to take part in a radical-radical reaction than the hexyl radical.



TABLE I.1

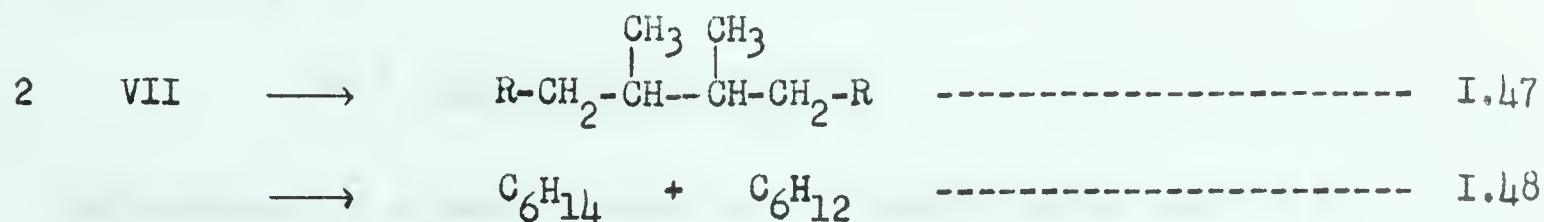
Estimated Reaction Rates for 1-Hexene Radiolysis

Reaction Type	Reaction Rate (mole/l sec)	
	Electron Irradiation (Dose rate = $1 \times 10^{20}$ ev/g min)	$\gamma$ -Irradiation (Dose rate = $1 \times 10^{18}$ ev/g min)
(i) Radical-radical reactions	$10^{-3}$	$10^{-6}$
(ii) Metathetical reaction	$10^{-4}$	$10^{-5}$
(iii) Radical addition to 1-hexene	$10^{-3}$	$10^{-4}$

The values obtained for the rates of the three processes are sufficiently close, at the dose rates considered, that none of the processes may be neglected in considering a free radical mechanism.

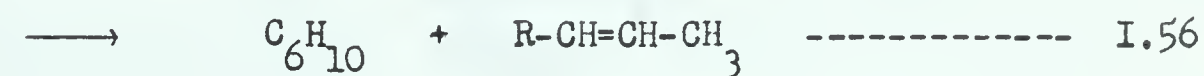
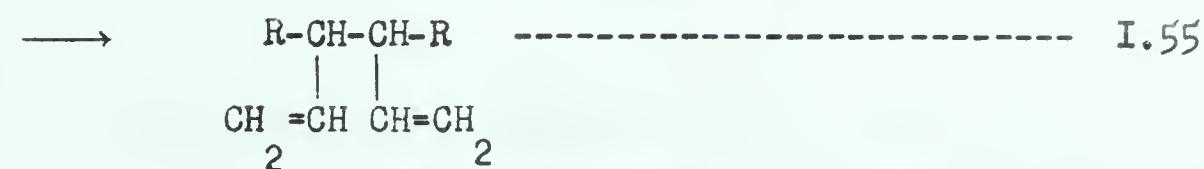
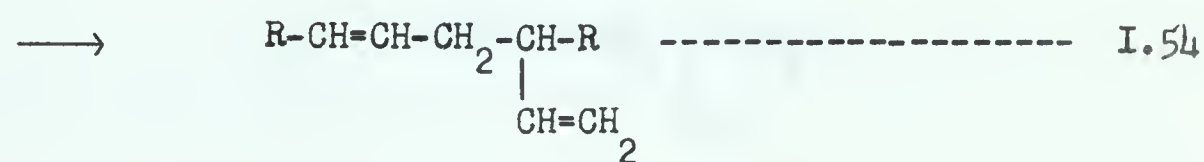
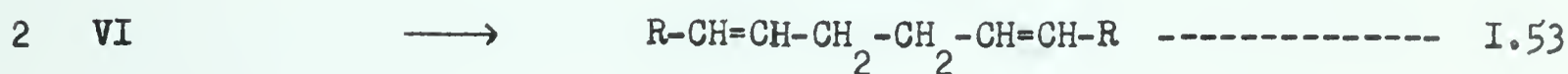
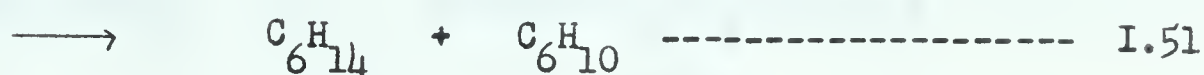
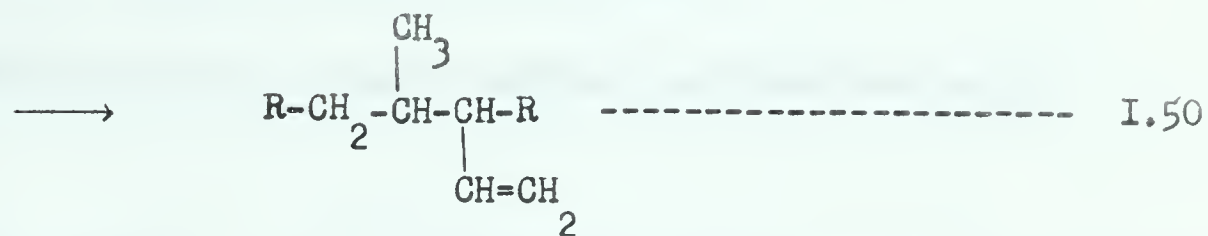
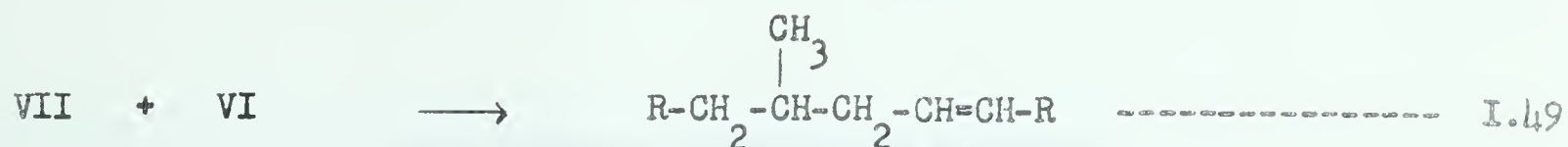
(i) Radical-Radical Reactions

The following radical-radical reactions may occur.





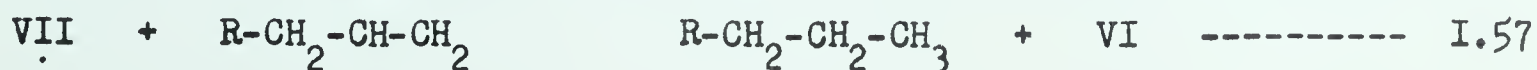




The hexene formed in steps I.48, I.52 and I.56 is assumed to be mostly 2-hexene, since this isomer is more stable than 1-hexene. Also, 2-octene is observed as one of the products in the reaction of free radicals with 1-octene (66).

### (ii) Metathetical Reaction

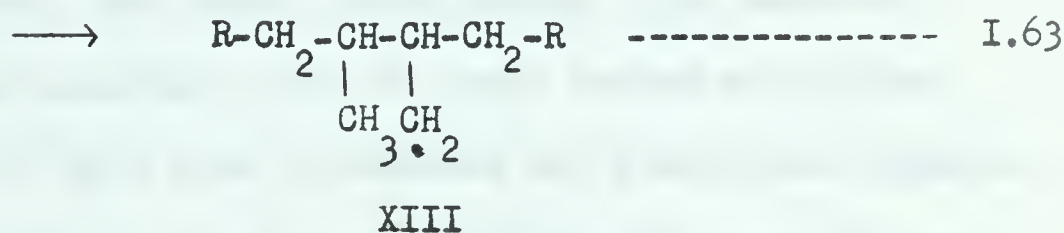
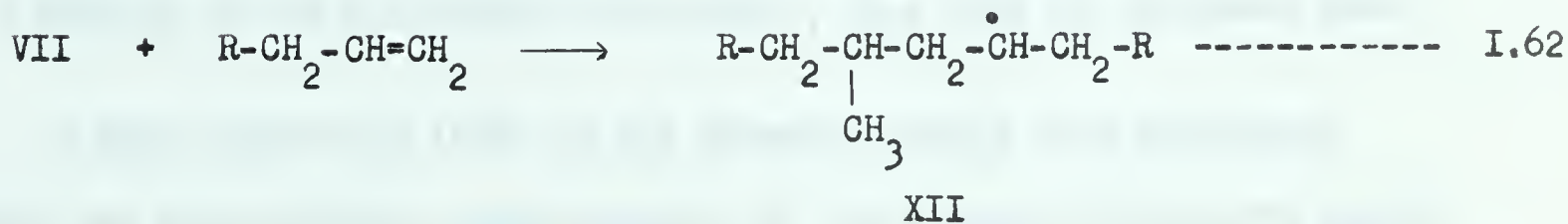
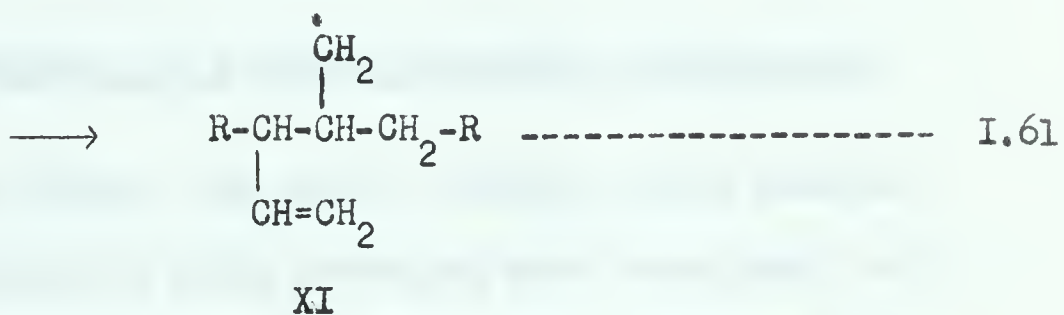
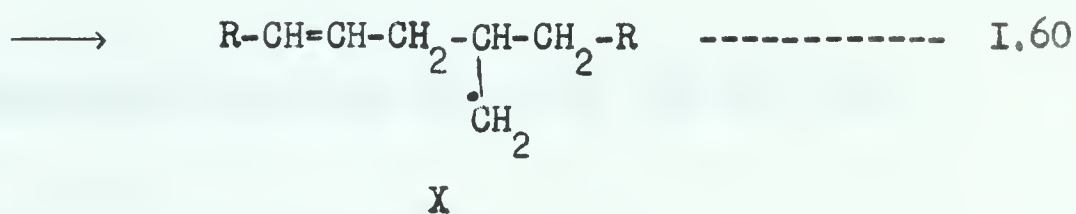
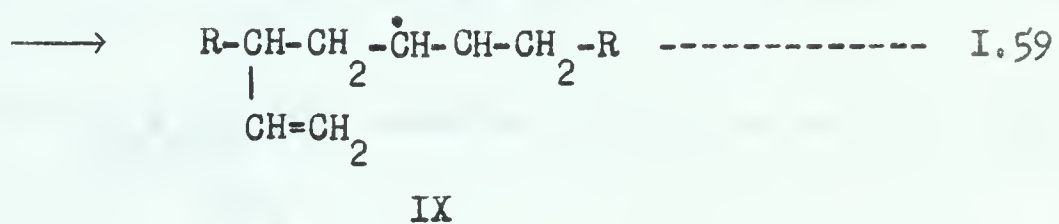
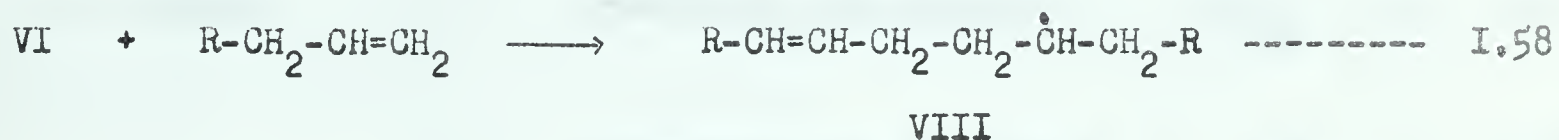
The reaction of a hexyl radical with 1-hexene gives rise to a hexenyl radical





(iii) Radical Addition to 1-Hexene

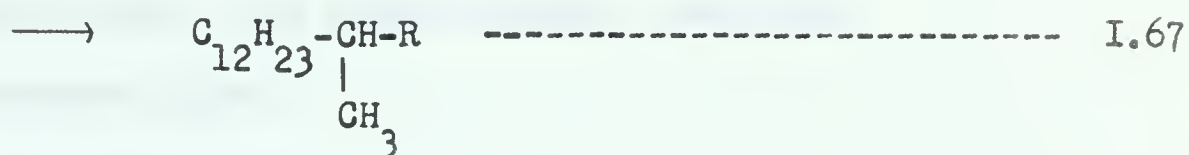
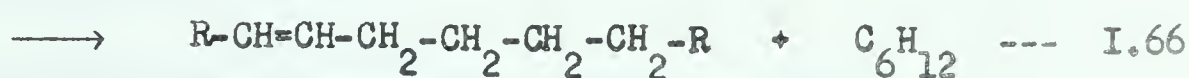
The following addition reactions between radicals and substrate might occur.







Subsequent reactions of species VIII might include



Similar reactions may be formulated for species IX, X, XI, XII and XIII.

### (3) Mechanisms for 1-Hexene Radiolytic Dimerization

The conclusion that 1-hexene, and similar straight chain terminal olefins, dimerized by a predominantly ionic mechanism when irradiated, was arrived at mainly from kinetic considerations. Since these considerations have a bearing on the cyclohexene radiolysis, they will be discussed here.

A high proportion (90%) of the dimeric product from irradiated 1-hexene was mono-olefinic, hydrogenation of the dimer fraction gave mainly n-dodecane and 5-methyl undecane, the former predominating. The nature of the dimer formed was therefore consistent with the ionic mechanism outlined above, since steps I.36 and I.37 give rise to dodecene and 5-methylene undecane, respectively. The conclusion that the 1-hexene dimerization proceeded by an



ionic mechanism did not arise solely because of this agreement however, but also because of the inability of a free radical mechanism to explain the nature of the measured radiolytic products. In particular the nature of the dimers formed, and the lack of isomerism to 2-hexene was said to be inconsistent (28) (67) with expected radical behaviour, and with the results of the radical induced reactions of 1-octene.

The free radical scheme cannot reasonably explain the high proportion of mono-olefinic dimer. The radical-radical reactions, I.47 - I.56, will be considered first.

Hexenyl radicals can be formed in the initial reaction steps I.42 and I.43, and also in the metathetical reaction I.57. Hexyl radicals can be formed in step I.44. The only radical-radical combination reactions that can yield mono-olefinic dimer are I.49 and I.50, involving a hexyl and a hexenyl radical. Thus to yield dimers that are 90% mono-olefinic the yield of hexyl radicals has to be  $> 82\%$  of the yield of hexenyl radicals. The yield of hexyl radicals (step I.13) cannot exceed the yield of hexenyl radicals in step I.42. Any production of hexenyl radicals in steps I.43 and I.57 is at the expense of the hexyl radical yield, so that the possibility of obtaining dimer that is 90% mono-olefinic is reduced or eliminated if reactions I.43 and I.57 are important. Even if a sufficient yield of hexyl radicals were available it is unreasonable to expect such a high proportion of dimer in the mono-olefinic form. This can be shown by the following argument.

The disproportion to combination rate constant ratio for two radicals A and B is defined as  $k_d / k_c = \nabla_{AB}$ . If it is assumed that





$\left(\nabla_{AB}\right) = \left(\nabla_{AA} \times \nabla_{BB}\right)^{\frac{1}{2}}$ , for the hexyl-hexenyl radical system,  
then for homogeneous kinetics we have that

$$\frac{[AB]}{\left([AA] \cdot [BB]\right)^{\frac{1}{2}}} = 2 \quad \text{----- I.68}$$

where  $[AB]$ ,  $[AA]$  and  $[BB]$  are the rates of formation of mono-olefinic, saturated and di-olefinic dimer, respectively.

If 90% of the dimer fraction is mono-olefinic, as is found experimentally, then expression I.68 has a value  $\gg 18$ . To obtain such a high value for this ratio, with a free radical mechanism, certain conditions would have to be met. Some such possible conditions will now be discussed.

If the disproportion combination ratio,  $\nabla$ , were much higher for reactions between two hexyl radicals,  $\left(\nabla_{AA}\right)$ , or between two hexenyl radicals,  $\left(\nabla_{BB}\right)$ , than for reactions between a hexyl radical and a hexenyl radical  $\left(\nabla_{AB}\right)$ , (i.e.  $\left(\nabla_{AA} \times \nabla_{BB}\right)^{\frac{1}{2}} \gg \nabla_{AB}$ ), then a high value for expression I.68 could be obtained. However the relationship  $\left(\nabla_{AA} \times \nabla_{BB}\right)^{\frac{1}{2}} = \nabla_{AB}$  seems much more probable, so this does not appear to be a reasonable condition.

Track and cage effects also fail to explain the high proportion of mono-olefinic dimer. An H-atom and a hexenyl radical can be formed in an initial homolytic cleavage (step I.42). If the H-atom added to a 1-hexene molecule in the cage surrounding the hexenyl radical, with a probability of unity, to give a hexyl radical, and this hexyl radical and the neighbouring hexenyl radical combined, then a mono-olefinic dimer would be the only dimeric product. However, since H-atom addition to a mono-olefinic has an activation





energy of  $\sim 5$  kcal/mole, and the H-atom is likely to diffuse out of the "cage" in a  $C_6$ -hydrocarbon system very readily, it seems unlikely that most of the dimer is formed by this cage process.

The possibility that radical addition to 1-hexene could give rise to the observed dimers will now be considered (see reactions I.58 - I.67, page 30 ). It must be assumed that this process predominates over radical-radical reactions, since it has already been shown that the latter type of reaction cannot explain the dimer distribution.

Addition of a hexyl radical gives rise to species XII and XIII which can only give mono-olefinic dimer by losing an H-atom in a radical-radical disproportionation reaction. Thus the hexyl addition process cannot yield the observed products under conditions where radical-radical reactions are unimportant.

Addition of hexenyl radicals to a 1-hexene might give rise to species VIII, IX, X and XI. Radical VIII can give rise to dodecane by reactions I.64 and I.66. Radical X can give rise to an olefin, which on hydrogenation would yield the 5-methyl undecane. Radicals IX and XI might yield mono-olefinic dimers but their structures do not coincide with those of the major radiolytic dimer products. Since radical addition is more probable at carbon atom 1 than at carbon atom 2 of an  $\alpha$ -olefin, structures VIII and IX might be expected to be the major products of hexenyl addition to 1-hexene. In such a case the dimers expected from this mechanism would not be those experimentally observed.

In summation, it appears that the conclusion is valid, that the



observed dimeric products from radiolysed 1-hexene cannot be readily explained by a free radical mechanism, although a more detailed analysis of all the dimers produced would make a more definite conclusion possible.

It will be seen that the distribution of dimeric products from radiolyzed cyclohexene contrasts markedly with the distribution of products from 1-hexene. The dimeric products from cyclohexene appear to be more consistent with the free radical scheme from a qualitative standpoint. The radiolyses of liquid 2-butene (68) and propylene (74) have been studied. If the arguments that were applied to the 1-hexene radiolytic system are applied to 2-butene and propylene radiolyses, then it appears that both the free radical and the ionic mechanisms are required to explain the complete distribution of products.

(d) Products Arising from C-C Bond Cleavage

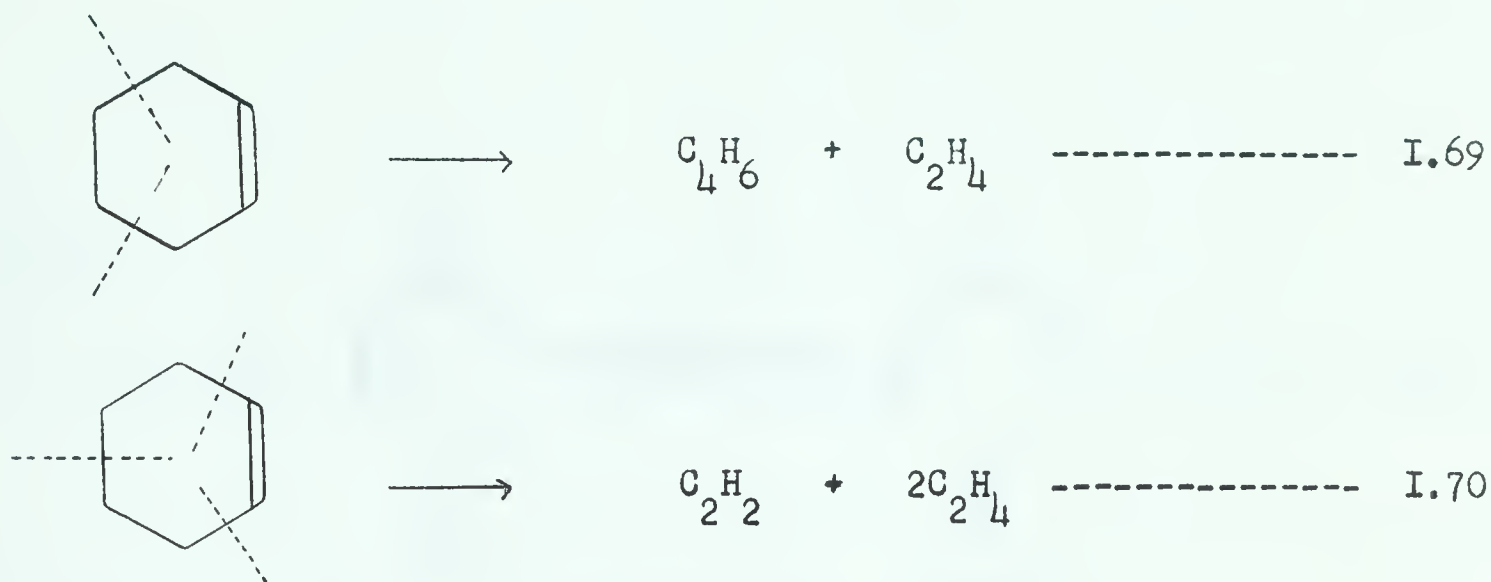
Not a great deal of attention has been applied to C-C bond cleavage in the radiolyses of non-cyclic olefins. The yields of fragmentation products reported for such systems were low relative to the yields of other products. (Hydrogen is not included as one of the fragments considered in this section). For example in the 1-hexene radiolysis a G-value of 0.024 was reported for fragmentation products, while  $G(-1\text{-hexene}) \approx 16$ .

In the radiolysis of liquid cyclohexene the yield of fragmentation products was only  $G = 0.28$  (75). The products were ethylene, acetylene and butadiene and were in proportions that were consistent with the reactions I.69 and I.70 below.



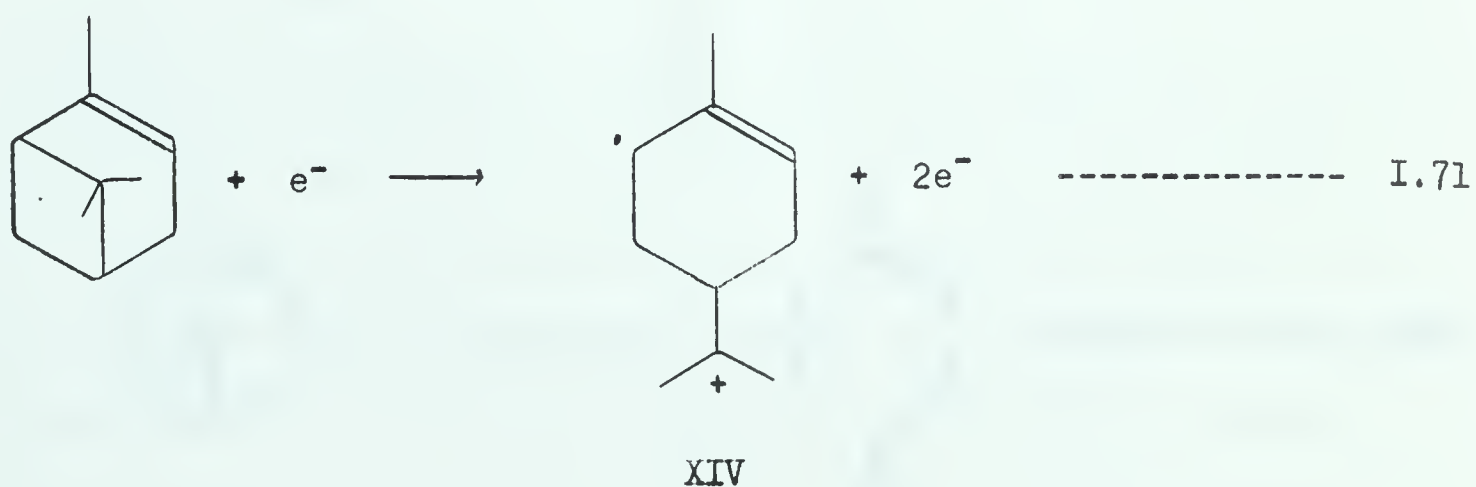




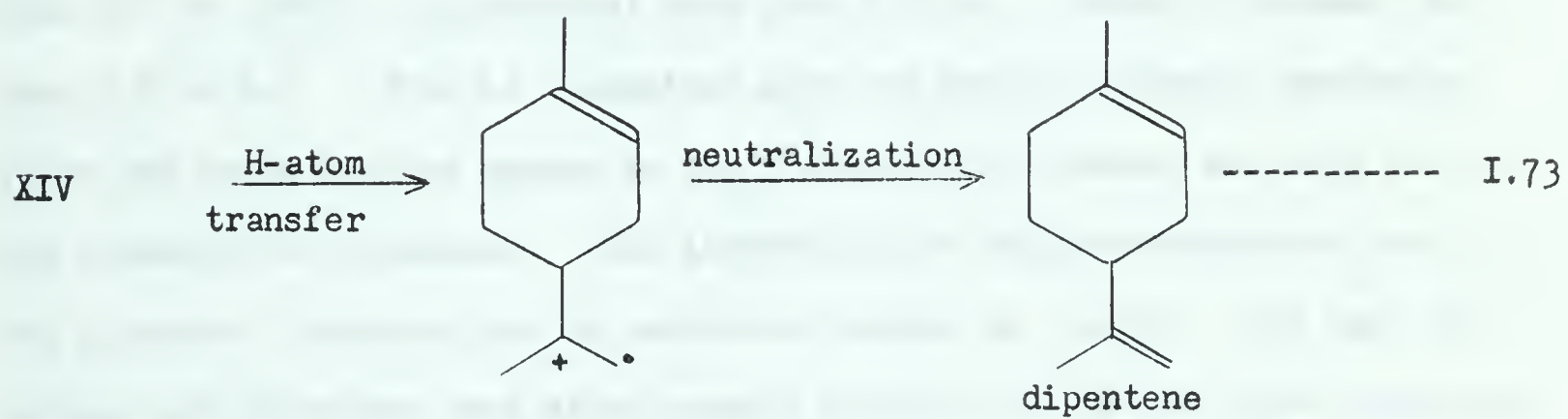
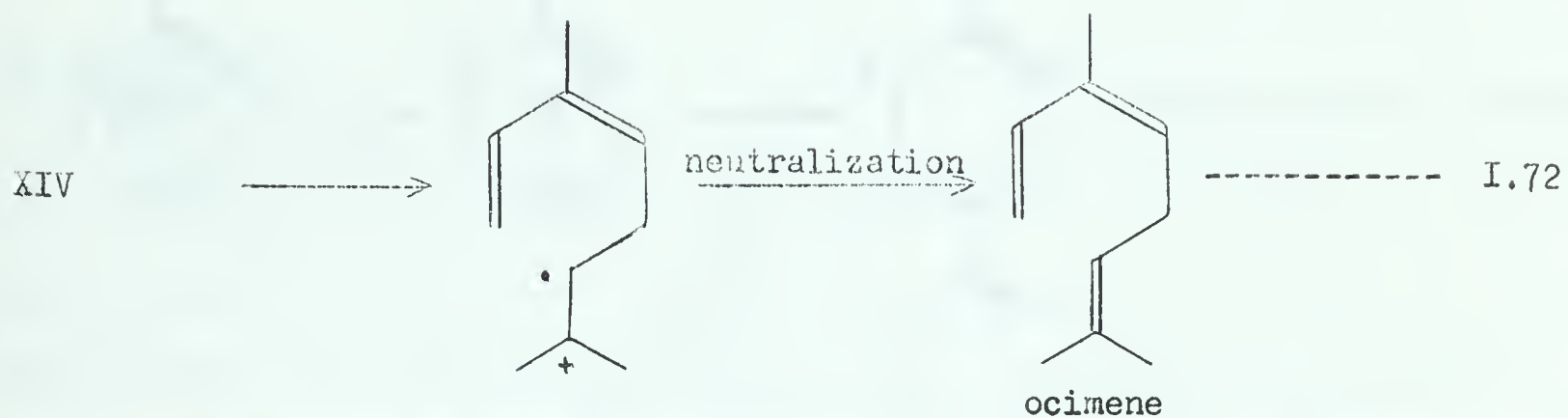


The formation of non-cyclic  $\text{C}_6$ -hydrocarbon products from cyclohexene was not exhaustively studied in the current work.

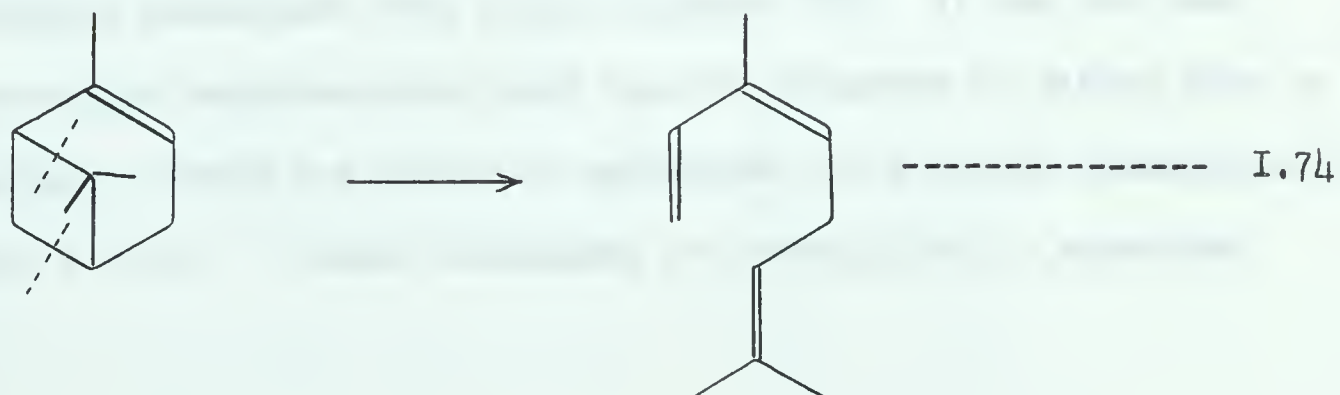
In the radiolysis of  $\alpha$ -pinene, ring opening was a major process (76). The presence of the cyclobutane ring in the molecule no doubt explains the instability of the ring structure under irradiation. Ocimene and dipentene were major products. Fragmentation, following ring opening, was a very minor process. Both excited and ionized  $\alpha$ -pinene molecules may give rise to these products. The processes suggested by Bates and Williams are given below. The ionic mechanisms are given by equations I.71, I.72 and I.73.







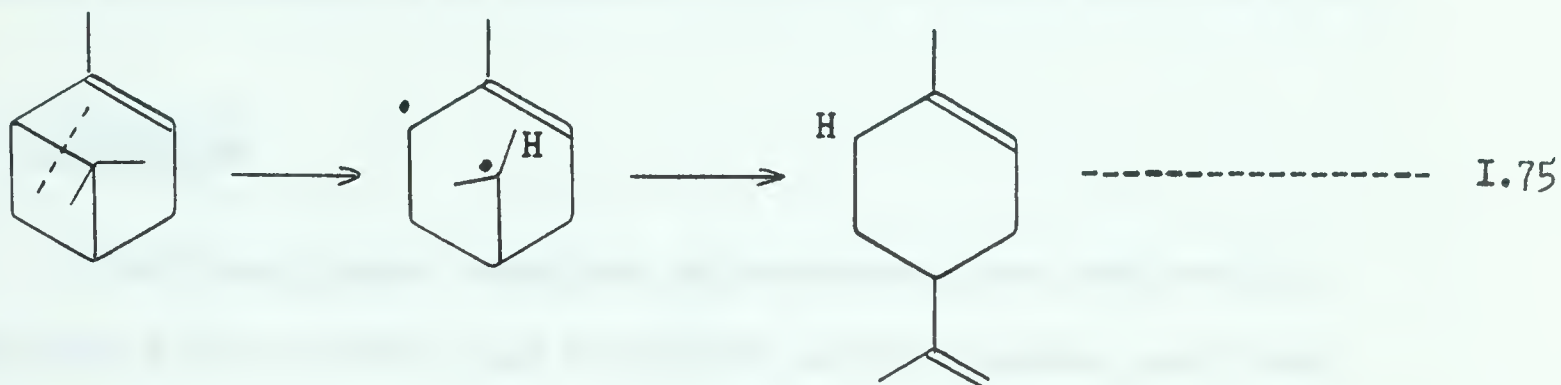
The excited molecule mechanisms for ocimene and dipentene formation from  $\alpha$ -pinene are





The reaction of 1-chloro-2-methylcyclohexanol with sodium hydroxide yields 1-methylcyclohexene.





When the temperature at which the radiolysis was carried out was lowered from 30° to -196°C, G(dipentene) rose from 0.9 to 1.3 while G(ocimene) fell from 2.2 to 0.8 . This is consistent with the excited molecule mechanism, since two bonds must be broken in the formation of ocimene, and only one in the formation of dipentene. (The intramolecular disproportionation step in the dipentene formation has an activation energy of  $\sim$ zero). The fact that ocimene and dipentene were major primary products in the gas phase pyrolysis of  $\alpha$ -pinene supports such a mechanism (77).

#### (e) Hydrogen Formation

G-values for hydrogen production in olefins, radiolyzed in the liquid phase, are usually and apparently always 2. This is in comparison to G-values of  $\sim 5$  for hydrogen production from liquid alkanes (78). It has not been possible to determine experimentally what type of mechanism is giving rise to hydrogen formation. Ionic and non-ionic mechanisms for hydrogen formation are given on pages 6 - 13 . Ionic mechanisms are exemplified by equations





The reaction was carried out in a round-bottomed flask equipped with a magnetic stirrer and a nitrogen inlet. The starting material (1.0 g, 4.0 mmol) was dissolved in 20 mL of dry THF. To this solution, a solution of the reagent (0.5 g, 4.0 mmol) in 10 mL of dry THF was added. The mixture was stirred at room temperature for 2 hours. The reaction was then quenched with 10 mL of water and extracted with 10 mL of ethyl acetate. The organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure. The resulting crude product was purified by column chromatography on silica gel using a gradient of 0 to 10% ethyl acetate in hexanes. The pure product was obtained as a white solid (0.3 g, 30% yield).

1H NMR (400 MHz, CDCl3)  $\delta$  7.2-7.4 (m, 4H), 6.8 (d, 2H), 4.5 (s, 2H), 3.8 (s, 3H).

High-resolution mass spectrometry (HRMS) was performed on the purified product. The calculated mass for the molecular formula  $C_{10}H_{10}O$  is 138.0726. The found mass is 138.0725. The mass spectrum shows a base peak at m/z 138.0726, corresponding to the molecular ion. The fragmentation pattern is consistent with the proposed structure of the product.

I.2, I.7, I.8 and I.10. Free radical and excited molecule reactions yielding hydrogen are illustrated by equations I.15, I.19, I.21, I.25 and I.26.

(f) Cyclohexene

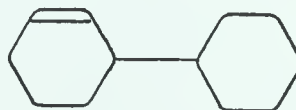
The liquid phase radiolysis of cyclohexene has been studied previously (75) (79) (80), and the nature of the products, and their distribution, were explainable in terms of free radical and excited molecule mechanisms.

For example, the dimeric products were dicyclohexyl, 3-cyclohexylcyclohexene and 2,2'-dicyclohexenyl\*. At a dose rate of  $\sim 10^{17}$  ev/g min for  $\gamma$ -radiolyses (75) (80) the G-values reported for these products were 0.11 - 0.15, 0.22 - 0.5, and 1.36 - 1.8 for dicyclohexyl, 3-cyclohexylcyclohexene and 2,2'-dicyclohexenyl respectively. An ionic mechanism of the type suggested earlier for 1-hexene dimerization (page 23) would yield 2-cyclohexylcyclohexene as the major dimeric product. This product was not formed (80). The formation of 2,2'-dicyclohexenyl as the major dimer indicated a free radical mechanism in which allylic type radicals were the most important intermediates.

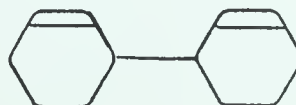
A detailed discussion of the cyclohexene radiolysis will be given in section IV.

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\* The 3-cyclohexylcyclohexene structure is



and the 2,2'-dicyclohexenyl structure is



Let  $f: X \rightarrow Y$  be a continuous map between topological spaces. Then the image of a closed set under  $f$  is not necessarily closed.

Example 1.1

Consider the map  $f: \mathbb{R} \rightarrow \mathbb{R}$  defined by  $f(x) = \sin(x)$ . The interval  $[0, \pi]$  is closed in  $\mathbb{R}$ , but its image  $f([0, \pi]) = [0, 1]$  is not closed in  $\mathbb{R}$ .

More generally, if  $f: X \rightarrow Y$  is a continuous map, then the image of a closed set  $A \subset X$  is closed in  $Y$  if and only if  $f$  is a closed map.

Proposition 1.2. Let  $f: X \rightarrow Y$  be a continuous map. Then  $f$  is a closed map if and only if for every closed set  $A \subset X$ , the set  $f(A)$  is closed in  $Y$ .

Proof. Suppose  $f$  is a closed map. Let  $A \subset X$  be a closed set. Then  $f(A)$  is closed in  $Y$  by definition.

Conversely, suppose that for every closed set  $A \subset X$ , the set  $f(A)$  is closed in  $Y$ . Let  $B \subset Y$  be a closed set. Then  $f^{-1}(B)$  is closed in  $X$  because  $f$  is continuous. Hence  $f(f^{-1}(B))$  is closed in  $Y$ . But  $f(f^{-1}(B)) \subset B$ , so  $B$  is closed in  $Y$ .



Figure 1.1: A diagram illustrating the concept of a closed map. It shows a set  $X$  with a subset  $A$ . A map  $f$  sends  $A$  to a subset  $f(A)$  of  $Y$ . The diagram shows that if  $A$  is closed in  $X$ , then  $f(A)$  is closed in  $Y$ .

(g) The Scope of the Present Work

It was pointed out earlier that in the radiolysis of cyclohexene the products were explained by a free radical mechanism. It was the intention in this work to formulate and carry out experiments to test the free radical explanation. Products formed as a result of C-H bond scission were the prime subject of study.  $\text{Co}^{60}$   $\gamma$ -rays were used throughout the work. The effects of dose, dose rate and additives on the yields of products from the radiolysis of liquid cyclohexene, were studied.

Some experiments were also carried out with deuterated cyclohexene.

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## SECTION II - EXPERIMENTAL



SECTION II    -    EXPERIMENTAL

(A)    MATERIALS

(a)    Compounds to be Radiolized

(1)    Cyclohexene

The cyclohexene, obtained from Eastman Organic Chemicals Co., was fractionally distilled through a 3' column at atmospheric pressure. The distillate contained 0.1% cyclohexane, and 0.008% of each of benzene and 1,3-cyclohexadiene. (The impurity concentrations are expressed as mole-percentages). This cyclohexene was irradiated without further treatment, for hydrogen yield determinations.

For all experiments where the cyclohexane yield was sought, the distilled cyclohexene was further purified by vapour phase chromatography (V.P.C.), using a  $2\frac{1}{2}$  metre, 20% by weight, di-n-decyl phthalate on firebrick, column. The cyclohexene was injected, 1 ml at a time, and trapped from the column before entering the Gow-Mac detector, since passage through the heated interior of this detector caused some decomposition of the olefin. The material was recycled through the column until the cyclohexane content was reduced to less than 0.02% .

For the attempt to detect 1,3-cyclohexadiene and benzene production, the cyclohexene was further purified through a column consisting of 2 metres of 30%, by weight, 3,3'-oxydipropionitrile on

CHAPTER 10

10.1

10.2

10.3

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The second part of the chapter discusses the importance of the...  
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firebrick, followed by a  $\frac{1}{2}$  metre of 25%, by weight, fluorolube on firebrick. Not more than 100  $\mu$ l of the cyclohexene could be injected at one time, without losing the separation between cyclohexene and 1,3-cyclohexadiene.

## (2) Cyclohexene-d<sub>10</sub>

The deuterated cyclohexene, as supplied by Merck, Sharp and Dohme of Canada Ltd., contained up to 12% C<sub>6</sub>D<sub>9</sub>H, depending upon the sample. The actual C<sub>6</sub>D<sub>9</sub>H content of the heavy cyclohexene used in a given experiment is given in the appropriate results section. Heavy cyclohexane (~0.3%) and benzene (~1.0%), were also present as impurities. No attempt was made to purify this material, except for the runs to determine liquid product yields from the radiolysis of heavy cyclohexene. In these cases the material was purified by V.P.C. as follows.

The cyclohexene-d<sub>10</sub> was first passed through the 3,3'-oxy-dipropionitrile/fluorolube column in 0.5 ml portions, to remove the benzene. It was then passed three times through the di-n-decyl phthalate column, injecting 0.7 ml at a time. This reduced the cyclohexane content to 0.012% .

## (3) 1,4-Cyclohexadiene

The 1,4-cyclohexadiene, as obtained from the Aldrich Chemical Co., Inc., contained 0.6% benzene, 0.8% 1,3-cyclohexadiene and 0.14% of each of cyclohexane and cyclohexene. The polymer content was negligible.





This material was used without further purification, except for the radiolysis of "pure" 1,4-cyclohexadiene. For this, the diene was purified by V.P.C., using the di-n-decyl phalate column. For the determination of G(benzene) and G(1,3-cyclohexadiene) the 1,4-diene was purified using the 3,3'-oxydipropionitrile/fluorolube column.

(4) 1,3-Cyclohexadiene

1,3-cyclohexadiene was obtained from Columbia Organic Chemicals Inc., and the Aldrich Chemical Co., Inc. After vacuum distillation to remove polymer, the Columbia material contained 11.8% 1,4-cyclohexadiene, 17.5% cyclohexene, and 2.9% benzene. After polymer removal, the Aldrich material contained 6.1% cyclohexene, 4.8% benzene, 0.1% 1,4-cyclohexadiene and 0.1% cyclohexane. For polymer yield determinations the Aldrich material was used without further purification.

For hydrogen yield determinations the Columbia 1,3-cyclohexadiene was used. It was purified by V.P.C., passing 100  $\mu$ l samples through the 3,3'-oxydipropionitrile/fluorolube column. The resulting material contained a total of about 1.0% of impurities, mainly cyclohexene and 1,4-cyclohexadiene.

The Aldrich material was used for the radiolysis of 1,3-cyclohexadiene - cyclohexene solutions to determine liquid product yields, for the appearance potential measurements, and for the



radiolysis of cyclohexene-d<sub>10</sub> - 1,3-cyclohexadiene solutions. For these purposes the 1,3-diene was purified with the use of the 3,3'-oxydipropionitrile/fluorolube column. 0.7 ml were injected at a time, and the material was recycled to reduce the impurities to a satisfactory level. The material finally contained 0.1% 1,4-cyclohexadiene, ~0% benzene and 2.5% cyclohexene.

#### (5) Benzene

Research grade benzene from the Phillips Petroleum Co. was used as supplied.

#### (b) Compounds Used for Identifications

Dicyclohexyl was supplied by the Aldrich Chemical Co., 1,1-dicyclohexenyl by Frinton Laboratories, diphenyl and phenyl cyclohexane by the Eastman Kodak Co., deuterium by General Dynamic Corp., 1,5-hexadiene by K and K Laboratories, cyclohexane by Fisher Scientific Co. and methane by Phillips Petroleum Co.

Isomers of cyclohexyl cyclohexene were prepared by heating phosphorous pentoxide with technical grade 2-cyclohexylcyclohexanol and 4-cyclohexylcyclohexanol (Eastman Organic Chemicals) and distilling the product in each case.

2,2'-dicyclohexenyl was prepared from cyclohexene, using the method described by Farmer and Moore (81). The di-tert-butyl peroxide (pract.) was supplied by Matheson, Coleman and Bell.





The dicyclohexadiene (tricyclo[4,4,2<sup>7,10</sup>,0] dodeca-2,8-diene) was prepared by heating 1,3-cyclohexadiene at 200°C for 20 hours in vacuo, (82) (83). A trace (<0.05 mole %) of diphenylpicrylhydrazil was added to the diene, in order to inhibit free radical processes.

(c) Materials Used for V.P.C.

Medium activity silica-gel and firebrick (30-60 mesh Kromat-FB) were obtained from the Burrell Corp., the silicone rubber emulsion from Wilkens Instrument and Research Inc., di-n-decyl-phalate (pract.) from Eastman Organic Chemicals, and 3,3'-oxydipropionitrile (pract.) from Matheson, Coleman and Bell.

(d) The  $\gamma$ -ray Source

The 300 curie Co<sup>60</sup>,  $\gamma$ -ray source was housed in a special irradiation room (cave).



(B) APPARATUS

(a) Vapour Phase Chromatography (V.P.C.) Unit

V.P.C. was used for the purification of the materials to be radiolized and for the analysis of products formed during irradiation. A description of the apparatus follows.

(1) The V.P.C. Unit

The V.P.C. unit is shown schematically in Figure II.1a. The hot wire detector (Model TR III B) and power supply (Model 9999-C) were manufactured by the Gow-Mac Instrument Co. and the recorder was manufactured by E.H. Sargent and Co. (Cat.No. S-72180). The columns were similar to the Burrell type,  $2\frac{1}{2}$  metre, heated U tube (Cat.No. 347-01-25). The column design was modified so that a dial thermometer (Fisher Scientific Co.) could be used to measure the temperature of the effluent gas. The column in use was enclosed in a box packed with glass wool.

Single stream operation was used, with helium as the carrier gas. The gas flow was controlled by the coarse valve, CV, and the fine valve FV (Edwards High Vacuum Ltd.). The coarse valve reduced the helium pressure to 16 lb/sq in. The flow rate was measured by the bubble flowmeter, F. The drying tube was packed with molecular sieve-13X (Burrell Corp.).

The detector was heated to  $425^{\circ}\text{F}$ . A detector current of 280 mA was used for analysis. The current was reduced to 150 mA during substrate purifications.

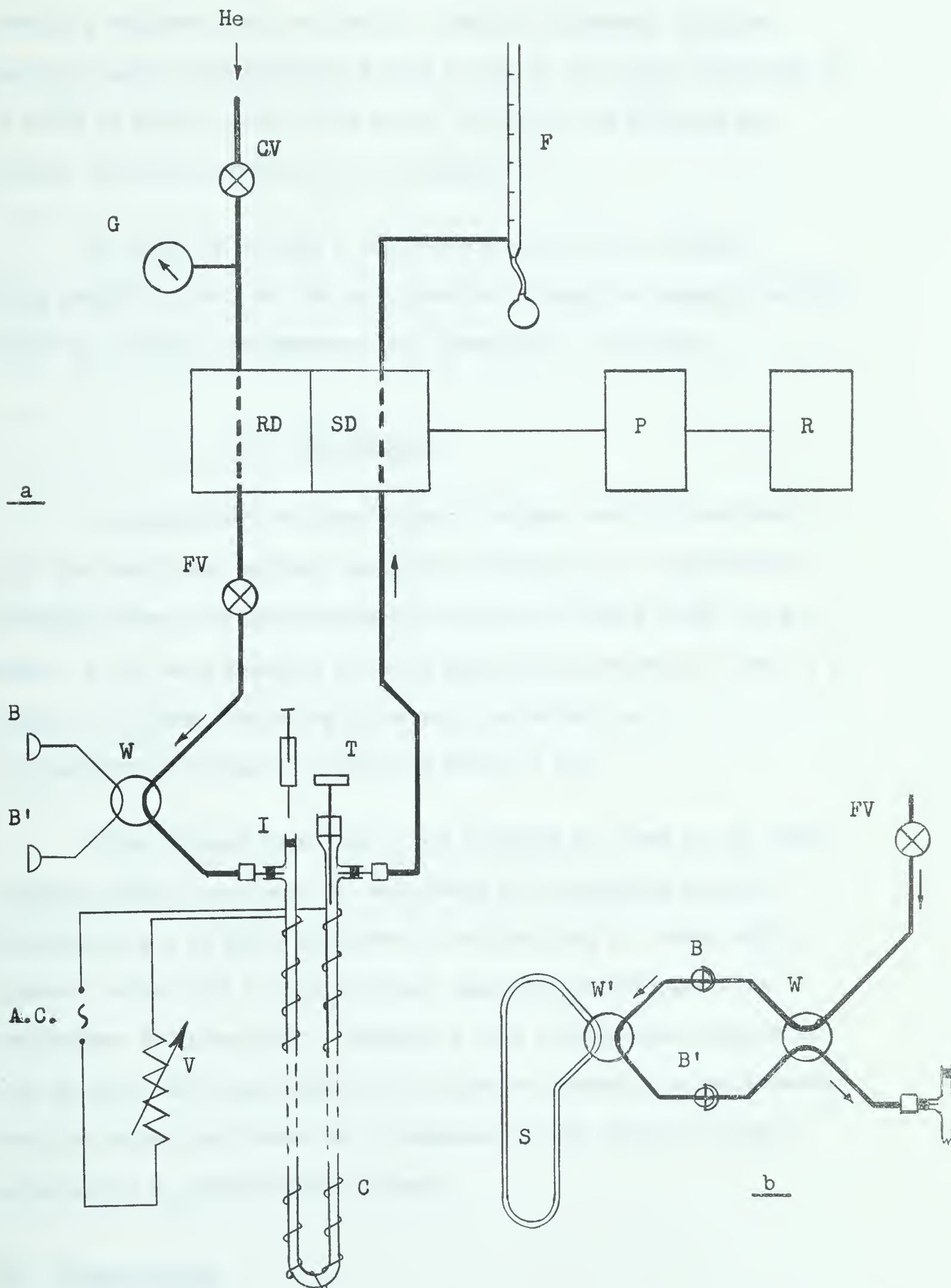
FIGURE II.1

a - Vapour Phase Chromatography Unit

He	Helium supply
CV	Flow control valve - coarse
FV	Flow control valve - fine
G	Pressure Gauge
W and W'	Four-way stop-cocks
B and B'	12/2 Ground glass ball joints
RD	Hot wire detector - reference side
SD	Hot wire detector - sample side
P	Gow-Mac power supply
R	Strip-chart recorder
C	Burrel type heated V.P.C. column
T	Dial thermometer
I	Liquid sample injection point
F	Bubble flowmeter
AC	A.C. power supply
V	Variac

b - Gas Sample Injection

S	Gas sample container
---	----------------------







Liquid samples were injected directly onto the column, through a silicone seal, at point I, using a hypodermic syringe. Gaseous samples were introduced from a trap at the 4-way stop-cock, W, as shown in Figure II.1b. The actual injection was effected by turning the 4-way stop-cock, W', through  $90^{\circ}$ .

In order to collect a separated product, or a material being purified, the gas flow was diverted through the opening normally sealed by the dial thermometer, and thence into a cold trap.

## (2) The Columns

A summary of the chromatography columns used in this work, with the conditions applied, is given in Table II.1. Approximate retention times, for hydrocarbons of interest in this study are also given. A far more complete study of hydrocarbon retention times on a number of columns, including di-n-decyl phthalate and 3,3'-oxydipropionitrile, is given by Hively (84).

Other columns were tried, and although not used in the final analysis scheme, some were of assistance in identifying products. Included were a  $7\frac{1}{2}$  metre silicone 550 column, and a 1 metre  $\text{AgNO}_3$  - glycerol column (85), both of which separated cyclohexane from cyclohexene satisfactorily. Apiezon L gave a separation similar to that given by silicone rubber, but tended to contaminate the detector when the column was heated to a temperature high enough to give a satisfactory  $\text{C}_{12}$ -hydrocarbon analysis.

### (b) Vacuum System

A vacuum system was used to prepare samples for irradiation and



to analyse irradiated samples for hydrogen and methane.

The system was constructed of Pyrex glass, and 4 mm bore stop-cocks, lubricated with silicone grease (Dow Corning), were used, except when otherwise stated. The main manifold is shown in Figure II.2. The system was evacuated by the mechanical vacuum pump (W.M. Welch Manufacturing Co.; Cat.No. 1405) and the mercury diffusion pump. The Pirani vacuum gauge, Type GP 110, was manufactured by Consolidated Electrodynamics. The traps  $T_1$  and  $T_2$  were immersed in liquid nitrogen whenever the system was in use. When the system was not in use, the 10 mm bore stop-cocks,  $M_1$  and  $M_2$ , greased with Apiezon N, were closed, while stop-cock 1 was opened to the atmosphere.

Stop-cock 3 connected the main manifold to the cell filling system, which will be described in the section on sample preparation (page 53 ).

Stop-cock 5 led to the gas analysis system, which will be described in the section on hydrogen-methane analysis (page 55 ).

FIGURE II.2

Main Vacuum Manifold

$M_1$ and $M_2$	10 mm stop-cocks
$T_1$ and $T_2$	Traps
1, 3 and 5	4 mm stop-cocks
MP	Welch Mechanical Vacuum Pump
DP	Mercury diffusion pump
P.G.	Pirani vacuum gauge
G.A.	Gas analysis manifold
C.F.	Sample preparation manifold



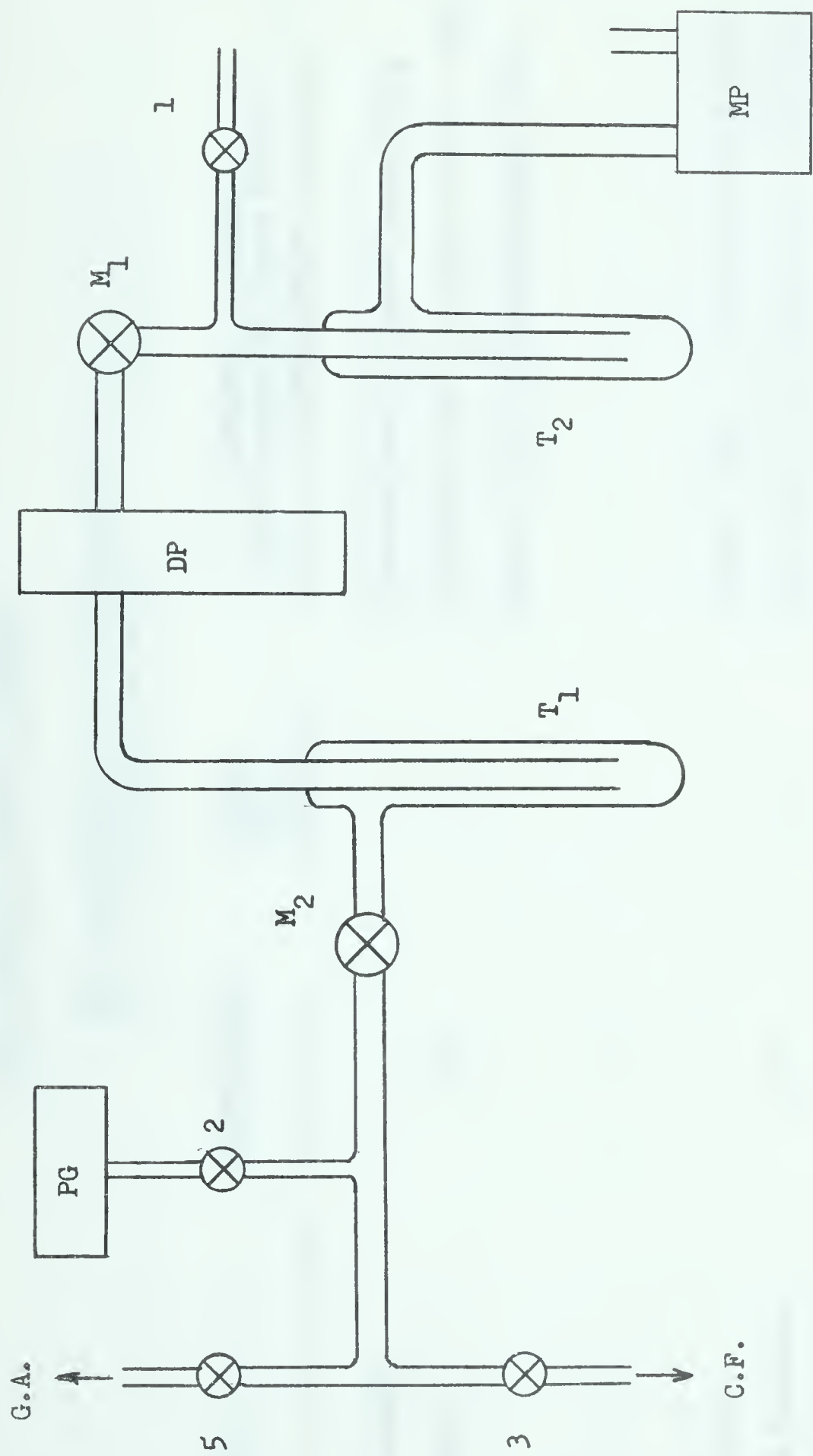




TABLE II.1

V.P.C. Columns Used for Analysis

The stationary phase concentrations are given in percentage by weight.

COLUMN	TEMPERATURE	HELIUM FLOW (ml/min.)	COMPOUNDS SEPARATED Approx. retention times (mins.) in parentheses
2½ metre, 20% di-n-decyl phthalate on firebrick	83°C	70	1,5-hexadiene (5); cyclohexane (9½); cyclohexene and 1,3-cyclohexadiene (13½); benzene (15); 1,4-cyclohexadiene (19).
2½ metre, 30% 3,3-oxy- dipropionitrile on firebrick	40°C	70	1-hexene (1½); 1,5-hexadiene (3); cyclo- hexane (2½); cyclohexene (7); 1,3-cyclo- hexadiene (13); 1,4-cyclohexadiene (20); benzene (30).
1 metre, activated charcoal	40°C	50	hydrogen (0.7); air (2.2); methane (7.3).



TABLE II.1 (Cont.)

COLUMN	TEMPERATURE	HELIUM FLOW (ml/min.)	COMPOUNDS SEPARATED Approx. retention times (mins.) in parentheses
2½ metre, 40% silicone Rubber*, on firebrick.	50 - 170°C in 11 mins.	70	C <sub>6</sub> -hydrocarbons (1½); n-decene and n-decane (5); n-dodecane (8); dicyclohexadiene (8½); dicyclic C <sub>12</sub> -hydrocarbons (9); tetradecane (10½).
2½ metre, medium activity silica-gel.	50 - 220°C in 16 mins.	100	cyclohexane, cyclohexene and 1,3-cyclo- hexadiene (5); benzene (6); 1,4-cyclo- hexadiene (6½); dicyclohexyl (13½); cyclohexylcyclohexene (15½); 2,2'-dicyclo- hexenyl (17); 1,1'-dicyclohexenyl and phenyl cyclohexene (20); biphenyl (23).

\* Based on the weight of the silicone rubber emulsion.





### (C) TECHNIQUES

#### (a) Sample Irradiation

The samples were irradiated using the 300 curie,  $\text{Co}^{60}$   $\gamma$ -ray source. A series of sample holders were available, at different distances from the source, for dose rate dependence studies. The dose rate at each position was measured using the "Fricke dosimeter" (86). A dose rate range of  $1 \times 10^{17} - 2 \times 10^{19}$  ev/ml hour was used. A Cary Recording Spectrophotometer (Model 14 M) was used to measure ferric ion formation in the Fricke dosimeter.  $[\epsilon (\text{Fe}^{3+}, 304 \text{ m}\mu, 25^\circ\text{C}) = 2225 ; G(\text{Fe}^{3+}) = 15.5]$ .

The liquid samples were degassed and then sealed into vacuum tight, Pyrex glass cells. For hydrogen yield determinations, 2 ml and 8 ml samples were irradiated. For the determinations of liquid product yields, 1 ml samples were irradiated. The preparation of these samples will be described in the next section.

#### (b) Sample Preparation

Samples to be irradiated were degassed and transferred into Pyrex glass cells using the section of the vacuum system shown in Figure II.3a. A sample was measured into the finger,  $F_1$ , by pipet. It was then degassed in the finger, using the conventional freezing-pumping-warming cycle, with stop-cock 4 being closed during the warming cycles. Degassing was completed during distillation of the sample from the finger to the trap  $T_3$ , with stop-cock 3, to vacuum, being open. The sample was

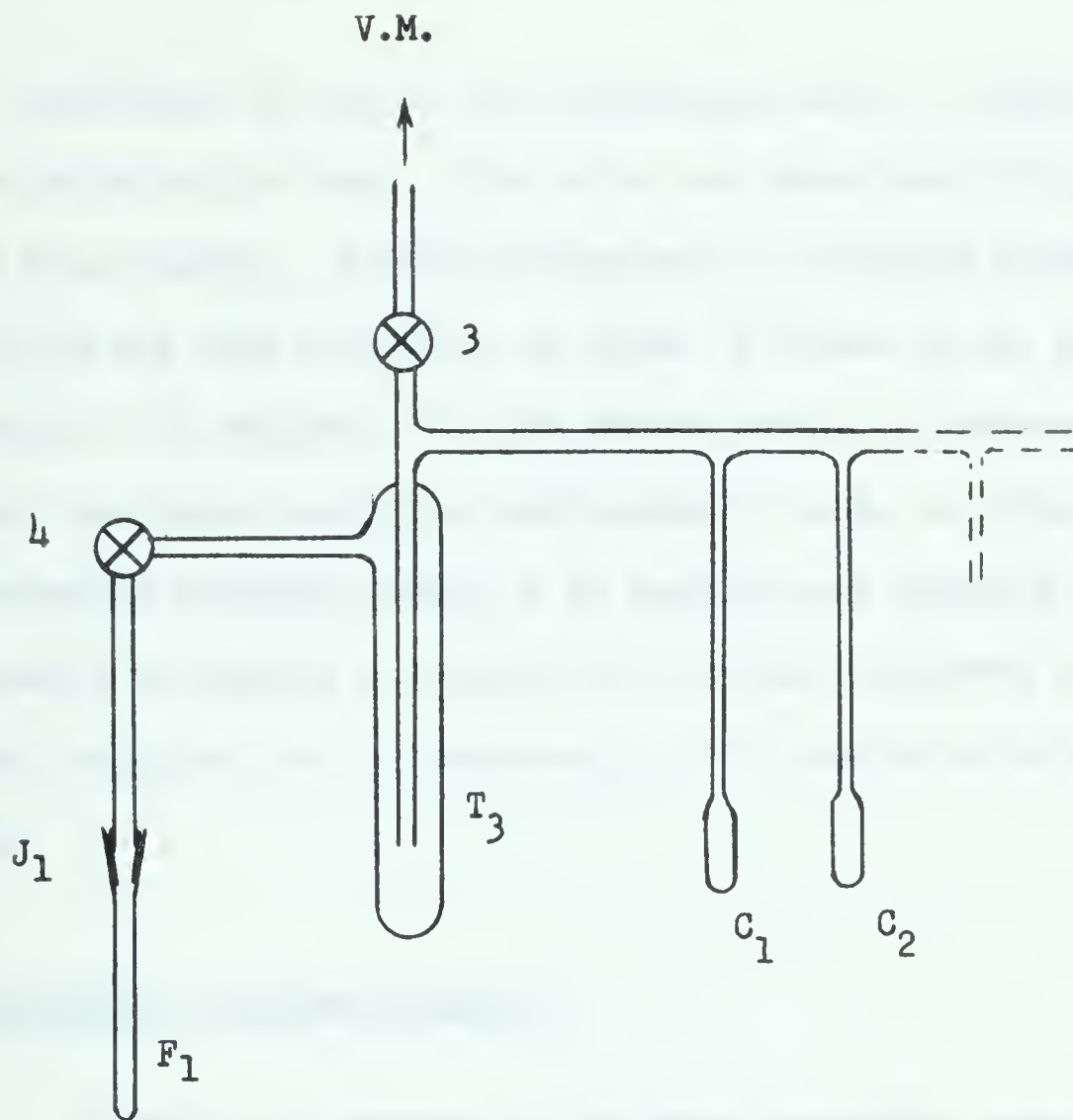
FIGURE II.3

a - Sample Preparation Manifold

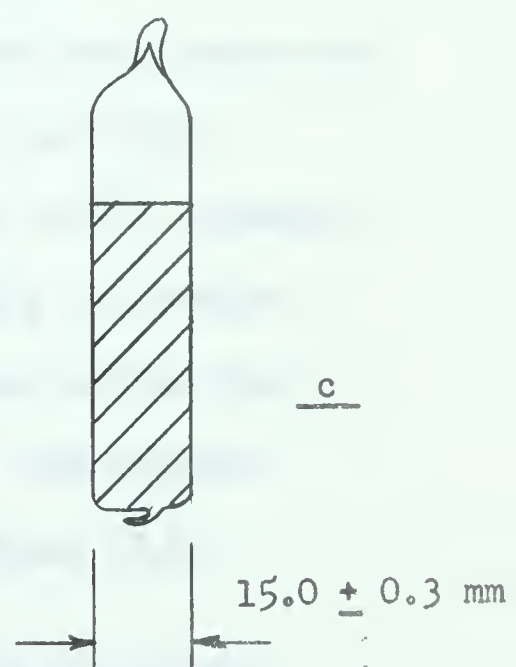
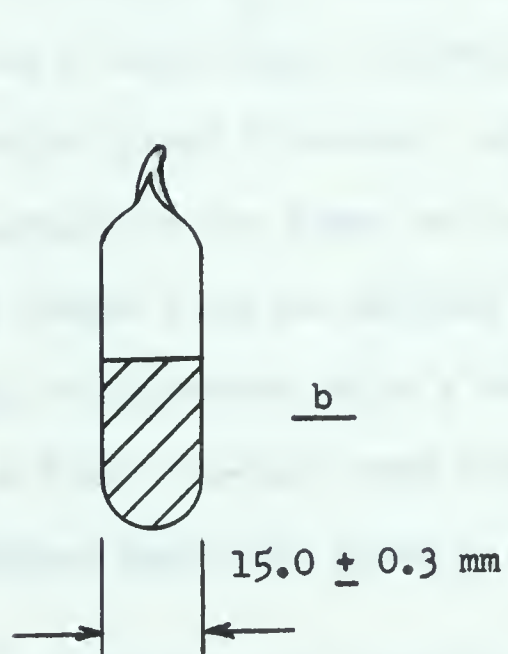
3 and 4	4 mm stop-cocks
J <sub>1</sub>	12/30 joint
F <sub>1</sub>	Finger for sample introduction
T <sub>3</sub>	Trap
C <sub>1</sub> and C <sub>2</sub>	Sample cells
V.M.	Main vacuum manifold

b - Sample Cell - Liquid Product Determinations

c - Sample Cell - H<sub>2</sub> and CH<sub>4</sub> Determinations



a







then transferred to one of the irradiation cells, C, which was then flame sealed at the neck. The cells were made from  $15.0 \pm 0.3$  mm O.D., Pyrex glass tubing. For the determination of liquid product yields the cells had test tube ends, as shown in Figure II.3b, and normally contained 1 ml samples. For the determination of hydrogen - methane yields, the tubes were made with breakable tips, as shown in Figure 3c. To determine hydrogen yields, 2 ml samples were normally irradiated, but some 8 ml samples were used for low dose radiolyses ( $\sim 3 \times 10^{18}$  ev/g). In the radiolysis of cyclohexene- $d_{10}$ , 1 ml samples were used in all cases.

#### (c) Hydrogen - Methane Analysis

Hydrogen and methane yields were determined using the gas analysis vacuum system shown in Figure II.4a. The irradiated sample cells were broken in finger  $F_2$ . Prior to breaking the cell, stop-cocks 5, 7 and 9 were closed and traps  $T_4$  and  $T_5$  and the finger were cooled to  $-196^\circ\text{C}$  with liquid nitrogen. After the cell was broken, stop-cock 7 was opened and the gases not condensable at  $-196^\circ\text{C}$  (hydrogen and methane) were pumped into the McCleod gauge, G, using the Toepler pump, P. The pump was operated using a subsidiary vacuum system that was evacuated by a Welch duo-seal pump (Cat.No. 1400). The measured volumes of the McCleod gauge are given in the key to Figure II.4b.

In order to determine the proportions of hydrogen and methane, a sample of the gas in the McCleod gauge was taken through stop-cock 9, to be analyzed by V.P.C., using the activated charcoal column.

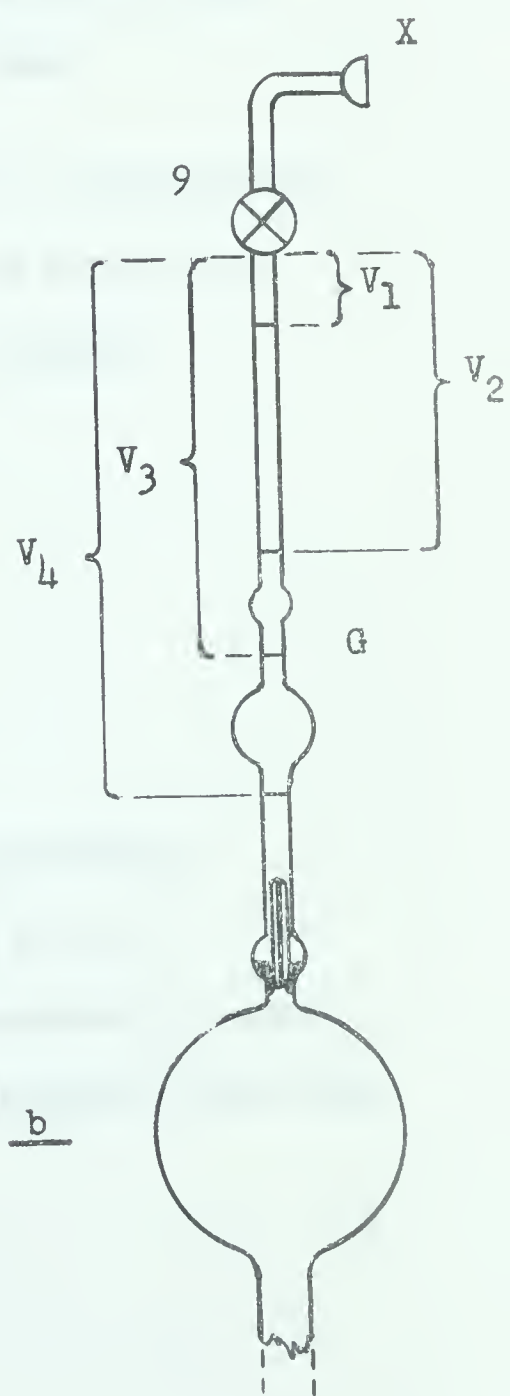
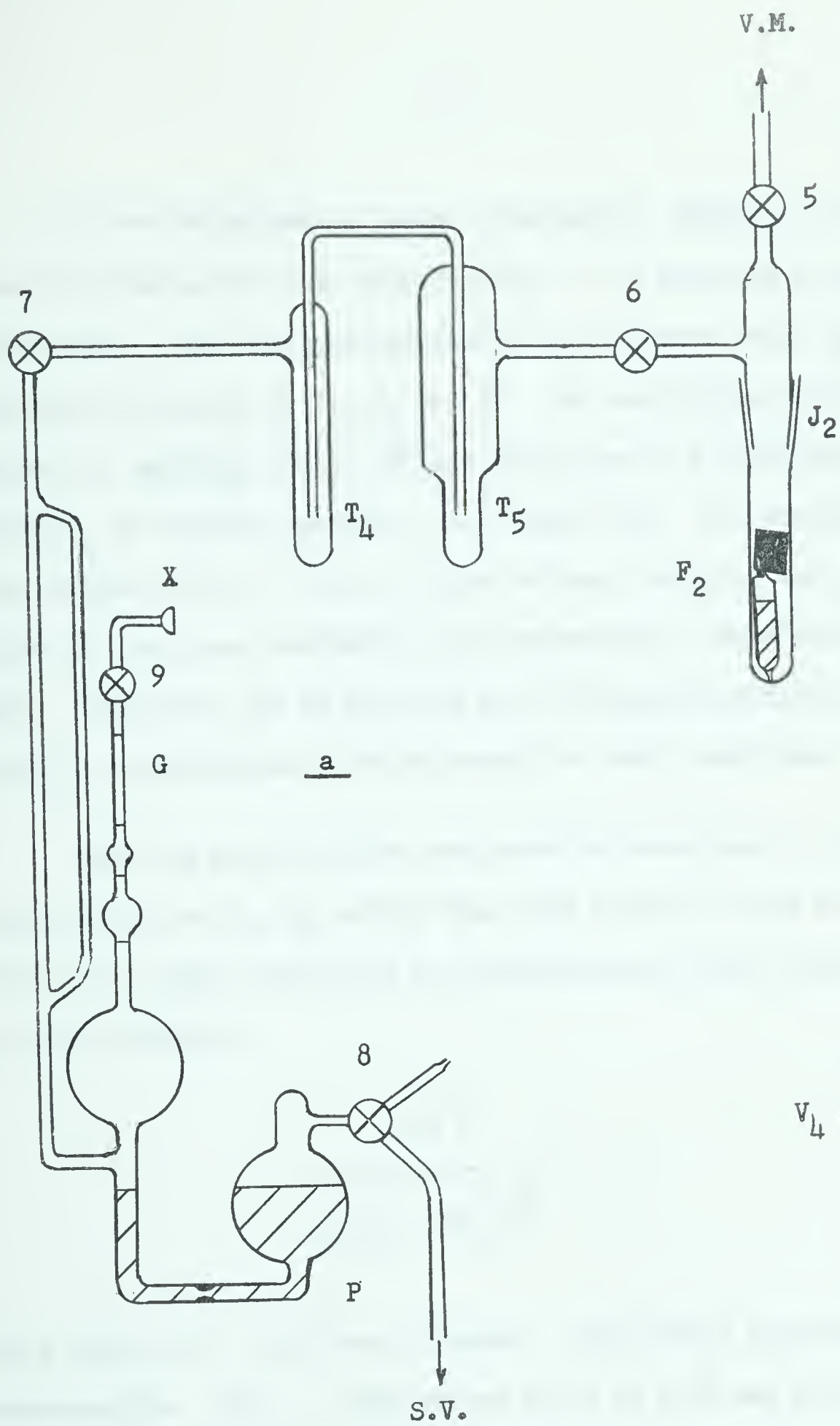
FIGURE II.4

a - H<sub>2</sub> and CH<sub>4</sub> Analysis System

J <sub>2</sub>	24/40 Joint introduction
F <sub>2</sub>	Sample finger
T <sub>4</sub> and T <sub>5</sub>	Traps
G	McCleod gauge
P	Teopler pump
S.V.	Subsidiary vacuum manifold
V.M.	Main vacuum manifold
5 - 8	4 mm stop-cocks
9	2 mm stop-cock
X	12/2 joint

b - McCleod Gauge - Calibrated Volumes

V <sub>1</sub>	0.220 cm <sup>3</sup>
V <sub>2</sub>	0.458 cm <sup>3</sup>
V <sub>3</sub>	1.119 cm <sup>3</sup>
V <sub>4</sub>	2.702 cm <sup>3</sup>





In the radiolysis of heavy cyclohexene, samples of the hydrogen formed were taken from the McCleod gauge to be analyzed by mass spectrometry. The mass spectrometer was calibrated using  $H_2$ ,  $D_2$  and an equilibrated mixture of  $H_2$ ,  $D_2$  and HD. The equilibrium mixture was obtained by applying a high voltage discharge to a 50/50 mixture of  $H_2$  and  $D_2$ , at reduced pressure, in a glass bulb. The sensitivities are given in Table II.2. Since the high voltage discharge was applied to the outside of the glass container, the temperature of equilibrium was not known. Therefore, the HD pressure was obtained by difference, using  $H_2$  and  $D_2$  sensitivities obtained under the same conditions.

When the sensitivities thus obtained were used to calculate the concentrations of  $H_2$ ,  $D_2$  and HD that were present in the equilibrium mixture, and these values for the concentrations were inserted into the expression

$$\frac{[HD]}{([H_2][D_2])^{\frac{1}{2}}} = Y$$

then a value of  $Y = 1.87$  was obtained. Theoretical equilibrium concentrations (87) gave values for  $Y$  of 1.86 and 1.91 at temperatures of  $110^\circ C$  and  $270^\circ C$ , respectively. This agreement, between the theoretical and experimental values of  $Y$ , was an indication that the hydrogen-deuterium calibrations were trustworthy.





TABLE II.2

H<sub>2</sub>, D<sub>2</sub>, HD Sensitivities for the Mass Spectrometer

COMPOUND	SENSITIVITY
<u>          </u>	<u>cm/micron</u>
H <sub>2</sub>	0.825
D <sub>2</sub>	1.12
HD	0.995

# THEORY

Let  $f(x)$  be a function defined on the interval  $[a, b]$ .

Function	Value
$f(x)$	$f(x)$
$f'(x)$	$f'(x)$
$f''(x)$	$f''(x)$
$f'''(x)$	$f'''(x)$

(d) Liquid Product Analysis

(1) Method

Liquid products were analyzed using V.P.C. Samples of 100  $\mu$ l were injected onto the silica-gel column, while 50  $\mu$ l samples were used with the other columns. A measure of the product concentrations relative to substrate concentration was obtained. Calibration of the V.P.C. is described below. The identity of the column used to measure any given product yield is included in the appropriate section of the results. (Section III).

(2) V.P.C. Calibration

The relative component concentrations of the solutions separated by V.P.C. were determined by measuring the areas under the peaks traced on the moving recorder chart. In order to relate relative areas to concentrations, calibration factors were determined. Calibrating solutions were made up with concentrations similar to those found in the irradiated samples. The solvent, which was always in large excess, was given a factor of unity, by definition. The calibration factor, P, for a given compound, x, when dissolved in solvent, y, is defined by

$$P = \frac{A_x (M_x + M_y)}{M_x (A_x + A_y)}$$

where  $A_x$  and  $A_y$  are the peak areas recorded for compounds x and y respectively, and  $M_x$  and  $M_y$  are the mole fractions of x and y, respectively,





in the solution being analyzed.

### (3) The Calibration Factors

The calibration factors obtained in this study are presented in Table II.3. Since the factors frequently varied with concentration, the results are also presented graphically in Figures II.5 - II.10 inclusive, as a function of solution composition. The compositions of the calibrating solutions are expressed by the ratio

Total peak area from the injected sample

---

Peak area due to solute being calibrated

The locations of the various graphs are included in Table II.3 for convenience.

### (e) Polymer Determination

Weighed samples of irradiated material (approx. 1.6 g) were evaporated by a stream of nitrogen, after a portion had been analyzed by V.P.C. for  $C_{12}$ -hydrocarbon content. The residue was weighed and then dissolved in a measured quantity of n-hexane. This hexane solution was then analyzed by V.P.C., first using the silicone rubber column to determine residual  $C_{12}$ -hydrocarbon and secondly using the di-n-decyl phthalate column to measure any residual  $C_6$ -hydrocarbon. Thus the weight of residue that was due to polymer was determined by difference.



TABLE II.3

Calibration Factors for Vapour Phase Chromatography

SOLVENT	SOLUTE	COLUMN PACKING	TOTAL AREA SOLUTE AREA	FACTOR	GRAPH LOCATION	
					PAGE	FIG.
Cyclo- hexene	Dicyclo- hexyl	Silica-Gel (medium activity)	2970	2.44	66	II.5B
			4560	2.26		
			4760	2.16		
			5800	2.39		
			6890	2.16		
			7160	2.23		
			7920	2.23		
			9100	2.19		
			9320	2.40		
			12500	2.26		
			25200	2.35		
<hr/>						
Cyclo- hexene	2,2'-Dicyclo- hexenyl	Silica-Gel (medium activity)	837	2.00	68	II.7D
			1420	1.86		
			1715	1.90		
			1850	1.94		
			3720	1.63		
			4400	1.70		



TABLE II.3 (Cont.)

SOLVENT	SOLUTE	COLUMN PACKING	<u>TOTAL AREA</u> SOLUTE AREA	FACTOR	<u>GRAPH LOCATION</u>	
					<u>PAGE</u>	<u>FIG.</u>
Cyclo- hexene	Cyclohexyl- cyclohexene	Silica-Gel (medium activity)	2820	1.75	66	II.5A
			5080	1.55		
			5510	1.78		
			9600	1.25		
			14200	1.51		
-----						
Cyclo- hexene	Cyclohexyl- cyclohexene	40% Silicone Rubber on Firebrick	755	1.86	70	II.9A
			1050	1.73		
			2135	1.47		
			5630	1.39		
-----						
Cyclo- hexene	Cyclohexane	20% Di-n-decyl Phthalate on Firebrick	505	0.94	69	II.8A
			576	1.07		
			1060	0.90		
			1650	1.01		
			2000	0.99		
			5320	1.01		





TABLE II.3 (Cont.)

SOLVENT	SOLUTE	COLUMN PACKING	$\frac{\text{TOTAL AREA}}{\text{SOLUTE AREA}}$	FACTOR	<u>GRAPH LOCATION</u>	
					PAGE	FIG.
50% Cyclo-hexene 50% Benzene	2,2'-Dicyclo-hexenyl	Silica-Gel (medium activity)	1360 2000 7260	1.56 1.48 1.24	68	II.7A
-----						
50% Cyclo-hexene 50% Benzene	2,2'-Dicyclo-hexenyl	40% Silicone Rubber on firebrick	868 1400	1.59 1.52	69	II.8D
-----						
50% Cyclo-hexene 50% 1,4-Cyclo-hexadiene	2,2'-Dicyclo-hexenyl	Silica-Gel (medium activity)	1628 5940	1.42 1.20	68	II.7B
-----						
50% Cyclo-hexene 50% 1,4-Cyclo-hexadiene	2,2'-Dicyclo-hexenyl	40% Silicone Rubber on firebrick	547 1660	1.56 1.39	69	II.8C



TABLE II.3 (Cont.)

SOLVENT	SOLUTE	COLUMN PACKING	TOTAL AREA SOLUTE AREA	FACTOR	GRAPH LOCATION	
					PAGE	FIG.
Cyclo- hexene	Dicyclo- hexyl	40% Silicone Rubber on Firebrick	138	1.89	67	II.6
			565	1.88		
			1140	1.79		
			1210	1.95		
			1760	1.60		
			2255	1.75		
			3140	1.49		
			4650	1.87		
			5470	1.88		
			5500	1.88		
<hr/>						
Cyclo- hexene	2,2'-Dicyclo- hexenyl	40% Silicone Rubber on Firebrick	195	1.76	70	II.9B
			1065	1.59		
			1160	1.75		
			1605	1.59		
			2320	1.41		
			2540	1.40		
			4900	1.53		

# Table 1.1

Year	1990	2000	2010	2020	2030
1990	100	100	100	100	100
2000	100	100	100	100	100
2010	100	100	100	100	100
2020	100	100	100	100	100
2030	100	100	100	100	100
2040	100	100	100	100	100
2050	100	100	100	100	100
2060	100	100	100	100	100
2070	100	100	100	100	100
2080	100	100	100	100	100
2090	100	100	100	100	100
2100	100	100	100	100	100
2110	100	100	100	100	100
2120	100	100	100	100	100
2130	100	100	100	100	100
2140	100	100	100	100	100
2150	100	100	100	100	100
2160	100	100	100	100	100
2170	100	100	100	100	100
2180	100	100	100	100	100
2190	100	100	100	100	100
2200	100	100	100	100	100
2210	100	100	100	100	100
2220	100	100	100	100	100
2230	100	100	100	100	100
2240	100	100	100	100	100
2250	100	100	100	100	100
2260	100	100	100	100	100
2270	100	100	100	100	100
2280	100	100	100	100	100
2290	100	100	100	100	100
2300	100	100	100	100	100
2310	100	100	100	100	100
2320	100	100	100	100	100
2330	100	100	100	100	100
2340	100	100	100	100	100
2350	100	100	100	100	100
2360	100	100	100	100	100
2370	100	100	100	100	100
2380	100	100	100	100	100
2390	100	100	100	100	100
2400	100	100	100	100	100
2410	100	100	100	100	100
2420	100	100	100	100	100
2430	100	100	100	100	100
2440	100	100	100	100	100
2450	100	100	100	100	100
2460	100	100	100	100	100
2470	100	100	100	100	100
2480	100	100	100	100	100
2490	100	100	100	100	100
2500	100	100	100	100	100
2510	100	100	100	100	100
2520	100	100	100	100	100
2530	100	100	100	100	100
2540	100	100	100	100	100
2550	100	100	100	100	100
2560	100	100	100	100	100
2570	100	100	100	100	100
2580	100	100	100	100	100
2590	100	100	100	100	100
2600	100	100	100	100	100
2610	100	100	100	100	100
2620	100	100	100	100	100
2630	100	100	100	100	100
2640	100	100	100	100	100
2650	100	100	100	100	100
2660	100	100	100	100	100
2670	100	100	100	100	100
2680	100	100	100	100	100
2690	100	100	100	100	100
2700	100	100	100	100	100
2710	100	100	100	100	100
2720	100	100	100	100	100
2730	100	100	100	100	100
2740	100	100	100	100	100
2750	100	100	100	100	100
2760	100	100	100	100	100
2770	100	100	100	100	100
2780	100	100	100	100	100
2790	100	100	100	100	100
2800	100	100	100	100	100
2810	100	100	100	100	100
2820	100	100	100	100	100
2830	100	100	100	100	100
2840	100	100	100	100	100
2850	100	100	100	100	100
2860	100	100	100	100	100
2870	100	100	100	100	100
2880	100	100	100	100	100
2890	100	100	100	100	100
2900	100	100	100	100	100
2910	100	100	100	100	100
2920	100	100	100	100	100
2930	100	100	100	100	100
2940	100	100	100	100	100
2950	100	100	100	100	100
2960	100	100	100	100	100
2970	100	100	100	100	100
2980	100	100	100	100	100
2990	100	100	100	100	100
3000	100	100	100	100	100



TABLE II.3 (Cont.)

SOLVENT	SOLUTE	COLUMN PACKING	TOTAL AREA SOLUTE AREA	FACTOR	GRAPH LOCATION	
					PAGE	FIG.
Cyclohexene	1,3-Cyclo- hexadiene	30% 3,3'-oxy- dipropionitrile	50.2	0.93	71	II.10B
			473	1.00		
			972	0.97		
			2210	1.00		
			6650	1.14		
-----						
Cyclohexene	1,4-Cyclo- hexadiene	30% 3,3'-oxy- dipropionitrile	183	1.00	71	II.10A
			1250	1.09		
			4420	0.97		
			6830	1.12		
-----						
1,4-Cyclo- hexadiene	2,2'-Dicyclo- hexenyl	Silica-Gel (medium activity)	1410	1.79	68	II.7C
			2840	1.63		
			3000	1.76		
-----						
1,4-Cyclo- hexadiene	2,2'-Dicyclo- hexenyl	40% Silicone Rubber on firebrick	830	1.53	69	II.8B
			3250	1.13		

FIGURE II.5

Calibration Factors

A

Solute:	Cyclohexylcyclohexene
Solvent:	Cyclohexene
Column:	Silica-gel

B

Solute:	Dicyclohexyl
Solvent:	Cyclohexene
Column:	Silica-gel

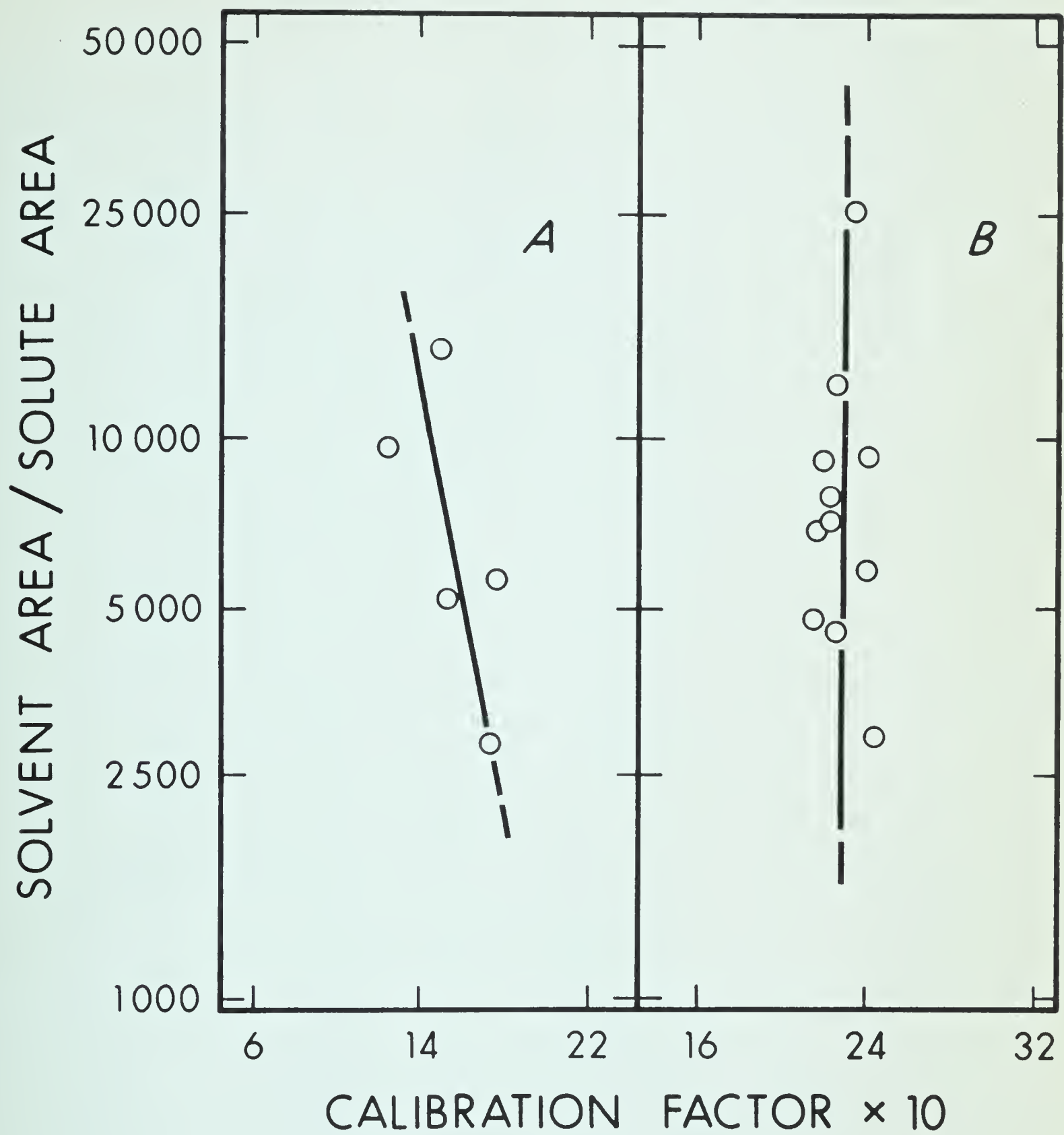


FIGURE II.6

Calibration Factors

Solute:	Dicyclohexyl
Solvent:	Cyclohexene
Column:	Silicone rubber

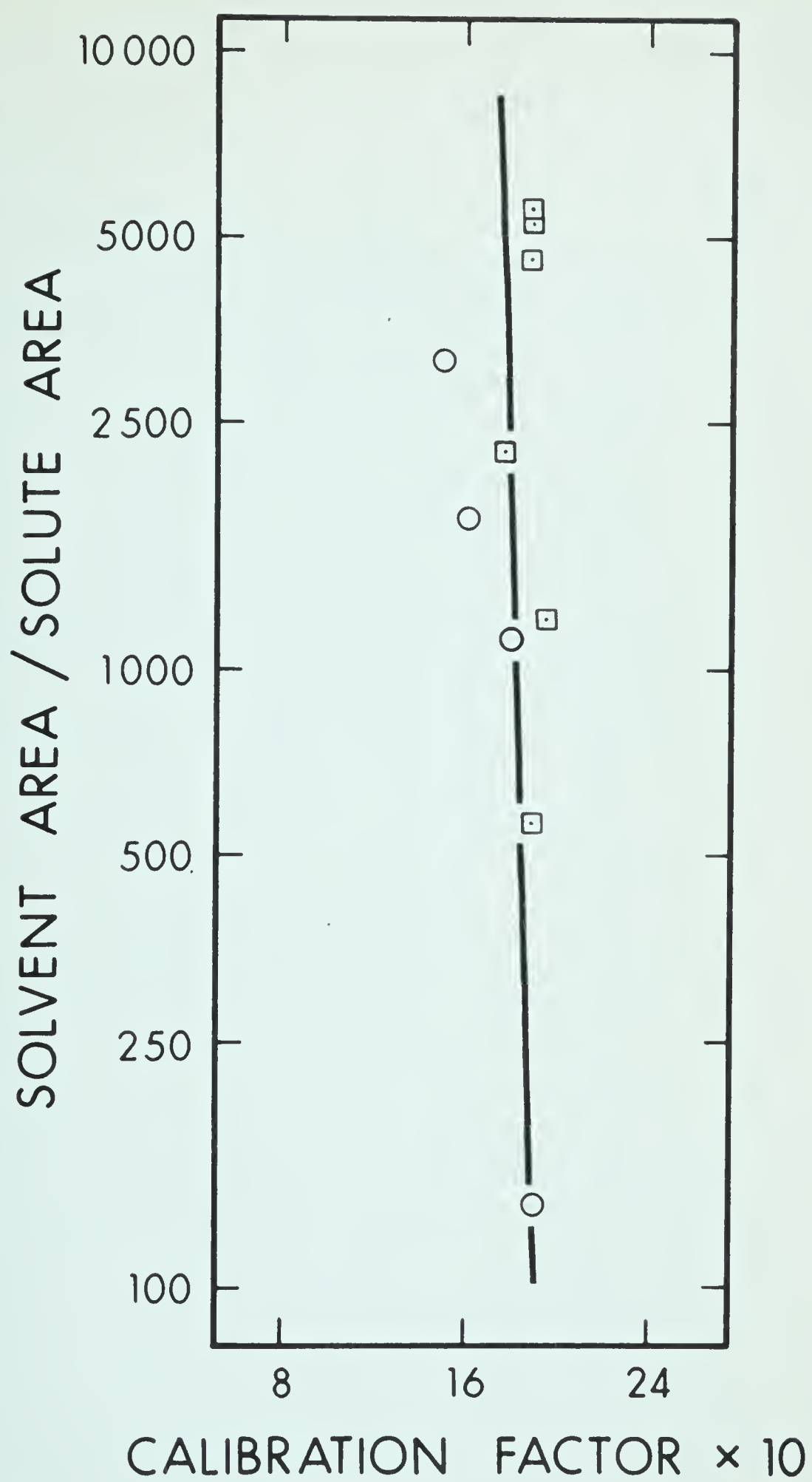




FIGURE II.7

Calibration Factors

A

Solute: 2,2'-dicyclohexenyl  
Solvent: 50/50 Cyclohexene and benzene  
Column: Silica-gel

B

Solute: 2,2'-dicyclohexenyl  
Solvent: 50/50 Cyclohexene and 1,4-cyclohexadiene  
Column: Silica-gel

C

Solute: 2,2'-dicyclohexenyl  
Solvent: 1,4-cyclohexadiene  
Column: Silica-gel

D

Solute: 2,2'-dicyclohexenyl  
Solvent: Cyclohexene  
Column: Silica-gel

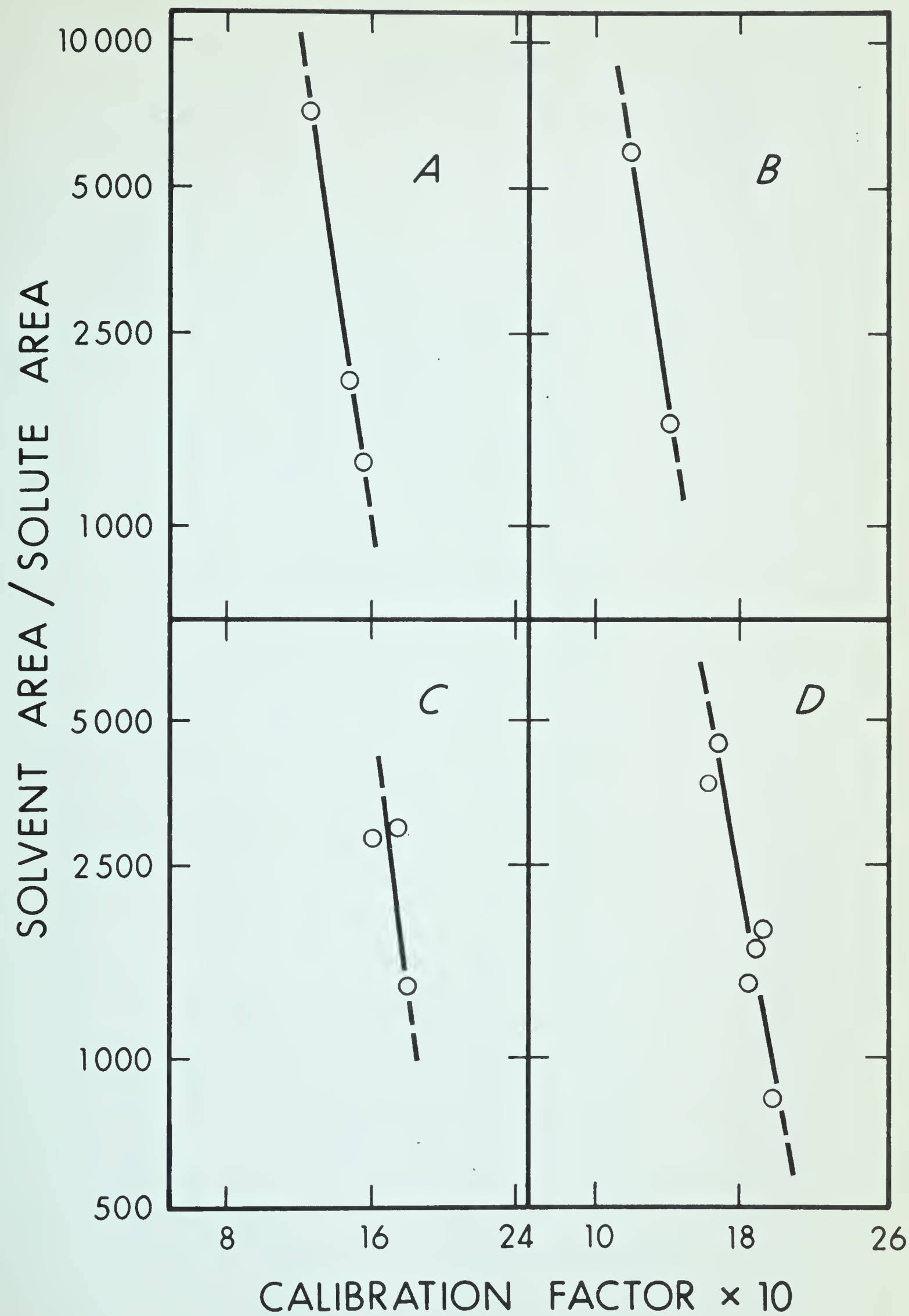


FIGURE II.8

Calibration Factors

A

Solute: Cyclohexane  
Solvent: Cyclohexene  
Column: Di-n-decyl phthalate

B

Solute: 2,2'-dicyclohexenyl  
Solvent: 1,4-cyclohexadiene  
Column: Silicone rubber

C

Solute: 2,2'-dicyclohexenyl  
Solvent: 50/50 Cyclohexene and 1,4-cyclohexadiene  
Column: Silicone rubber

D

Solute: 2,2'-Dicyclohexenyl  
Solvent: 50/50 Cyclohexene and benzene  
Column: Silicone rubber

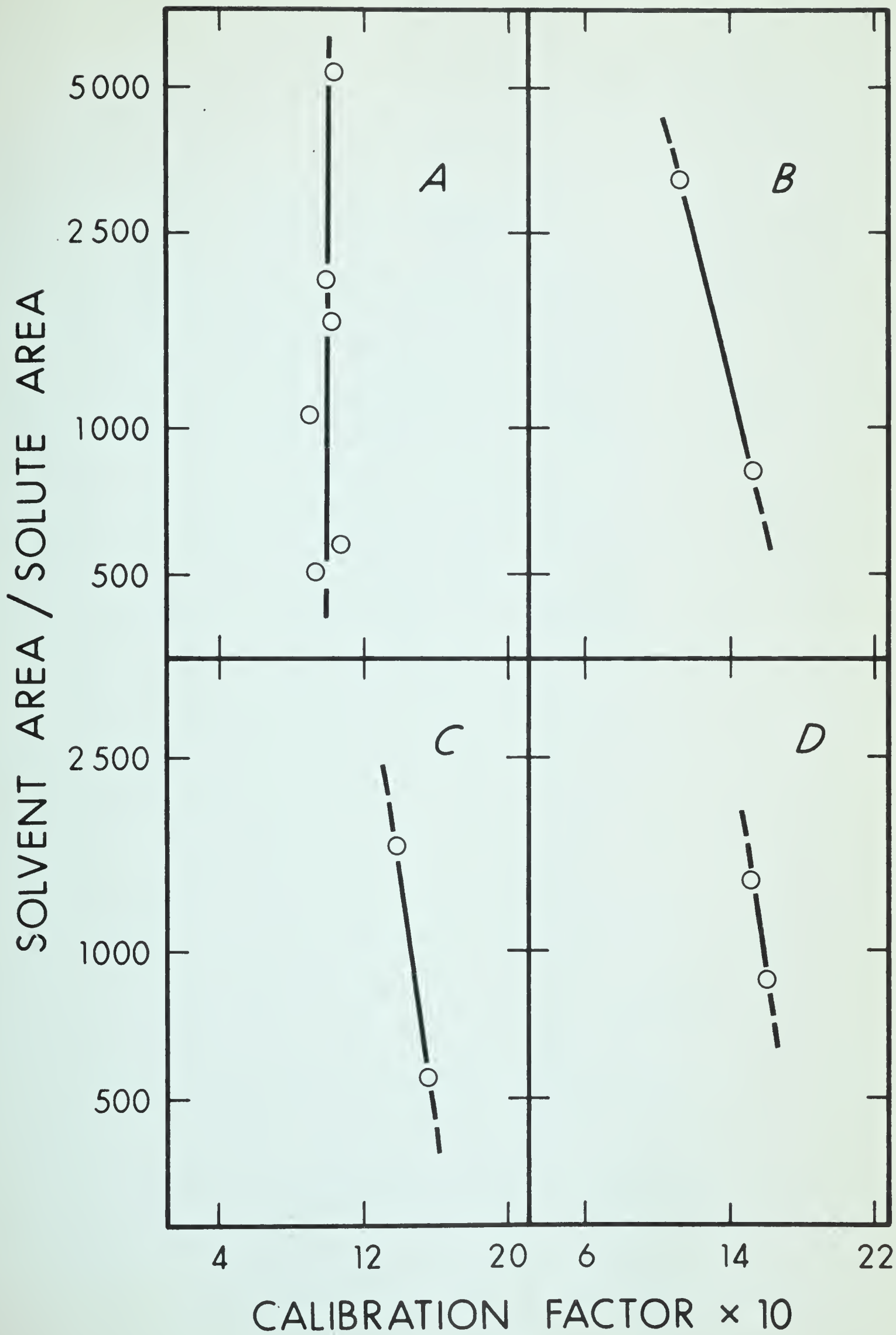


FIGURE II.9

Calibration Factors

A

Solute:	Cyclohexylcyclohexene
Solvent:	Cyclohexene
Column:	Silicone rubber

B

Solute:	2,2'-dicyclohexenyl
Solvent:	Cyclohexene
Column:	Silicone rubber



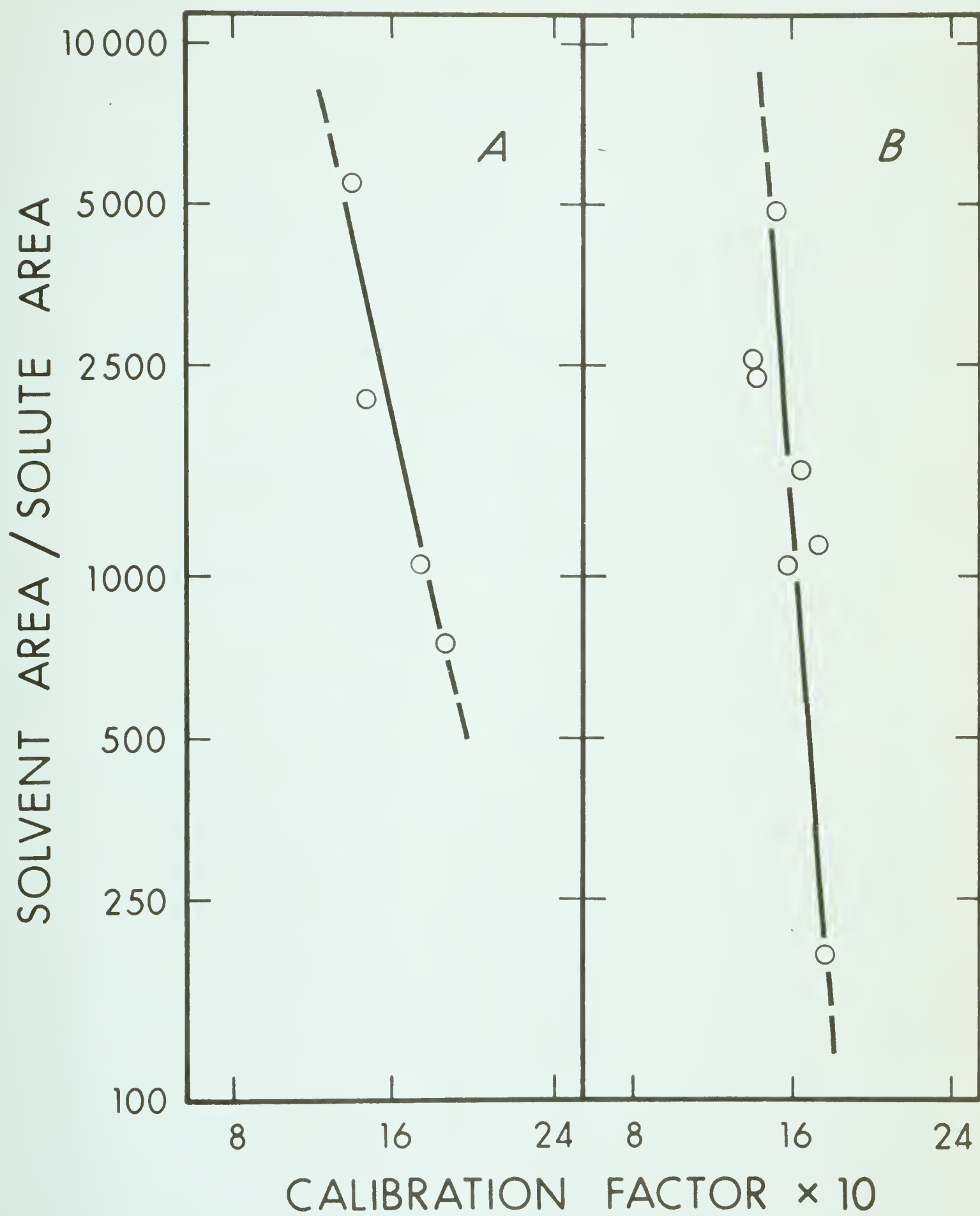


FIGURE II.10

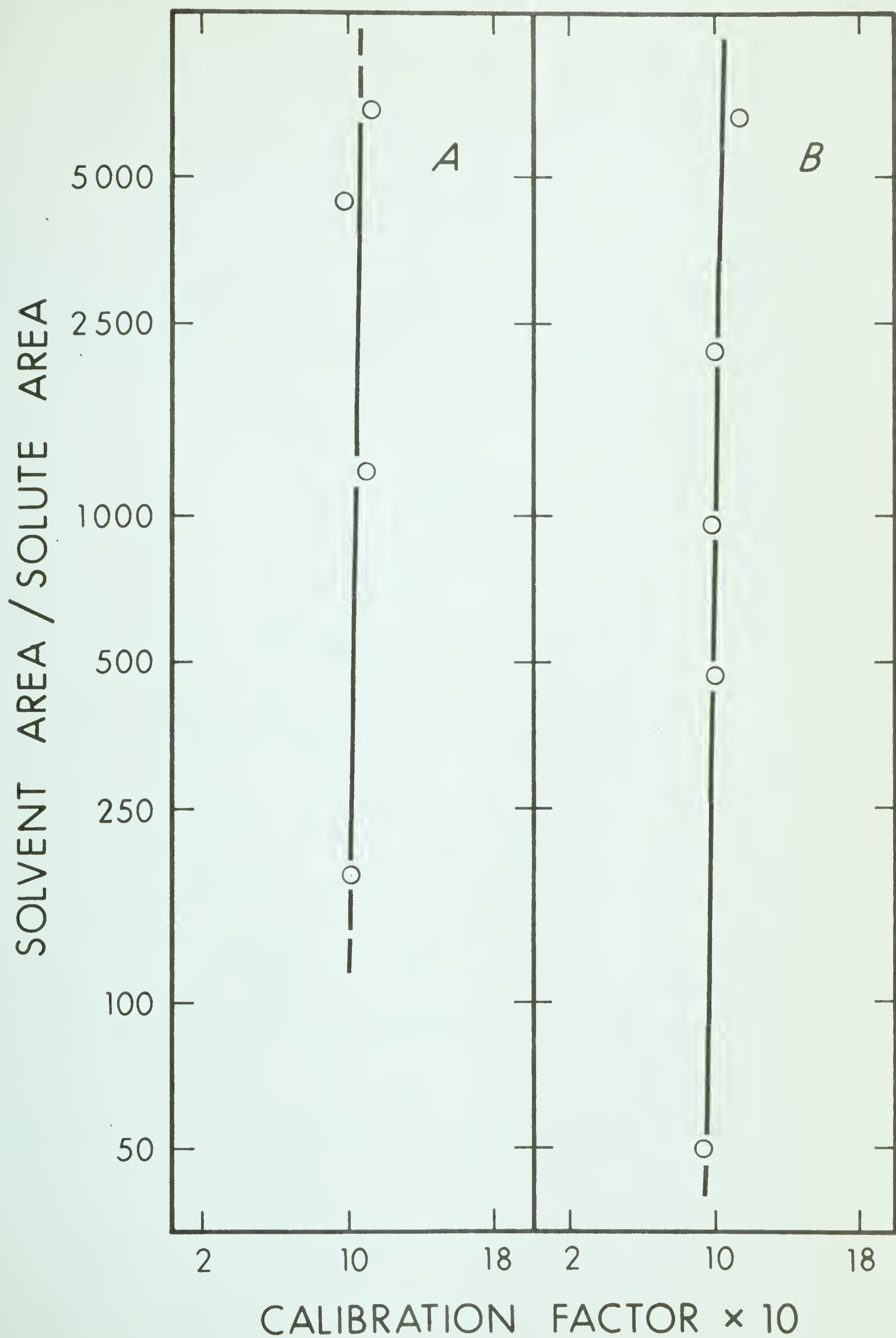
Calibration Factors

A

Solute: 1,4-cyclohexadiene  
Solvent: Cyclohexene  
Column: 3,3'-oxydipropionitrile

B

Solute: 1,3-cyclohexadiene  
Solvent: Cyclohexene  
Column: 3,3'-oxydipropionitrile



(f) Product Identification

(1) Cyclohexane

The product identified as cyclohexane was eluted from four different V.P.C. columns with the correct retention time, and a sample of this product, trapped from the di-n-decyl phthalate column, gave a parent mass of 84 on the mass spectrometer.

(2) Dimers

(i) Method

The identification of dimers was based on their retention times on the silica-gel and the silicone rubber columns. Figures II.11 and II.12 give a number of V.P.C. records obtained from the silica-gel and silicone rubber columns, respectively. Line (i) in Figure II.11 gives retention times on silica-gel, and line (i) in Figure II.12 gives retention times on silicone rubber, for a number of pure compounds. It appeared that the temperature programming of silicone rubber gave separations on the basis of boiling point, while the retention times on temperature programmed silica-gel were influenced by boiling point, structure and degree of unsaturation. Before considering the identity of the radiolysis products, the analysis of some of the compounds used to establish these retention times will be discussed.

(ii) Analysis of Standard Materials

The material supplied as dicyclohexyl gave a single peak from





FIGURE II.11

V.P.C. Records - Silica-Gel Column

(i) Authentic Compounds

1. 1-Decene
2. Dicyclohexyl
3. Prepared cyclohexylcyclohexene
4. Dicyclohexadiene
5. 2,2'-Dicyclohexenyl
6. 1,1'-Dicyclohexenyl and phenyl cyclohexane
7. Biphenyl

(ii) Irradiated cyclohexene

(iii) Irradiated solution of 0.2% 1,3-cyclohexadiene in cyclohexene

(iv) Irradiated solution of 2% 1,4-cyclohexadiene in cyclohexene

(v) Irradiated solution of 10% 1,4-cyclohexadiene in cyclohexene

(vi) Irradiated 1,4-cyclohexadiene

(vii) Products from preparation P<sub>2</sub>

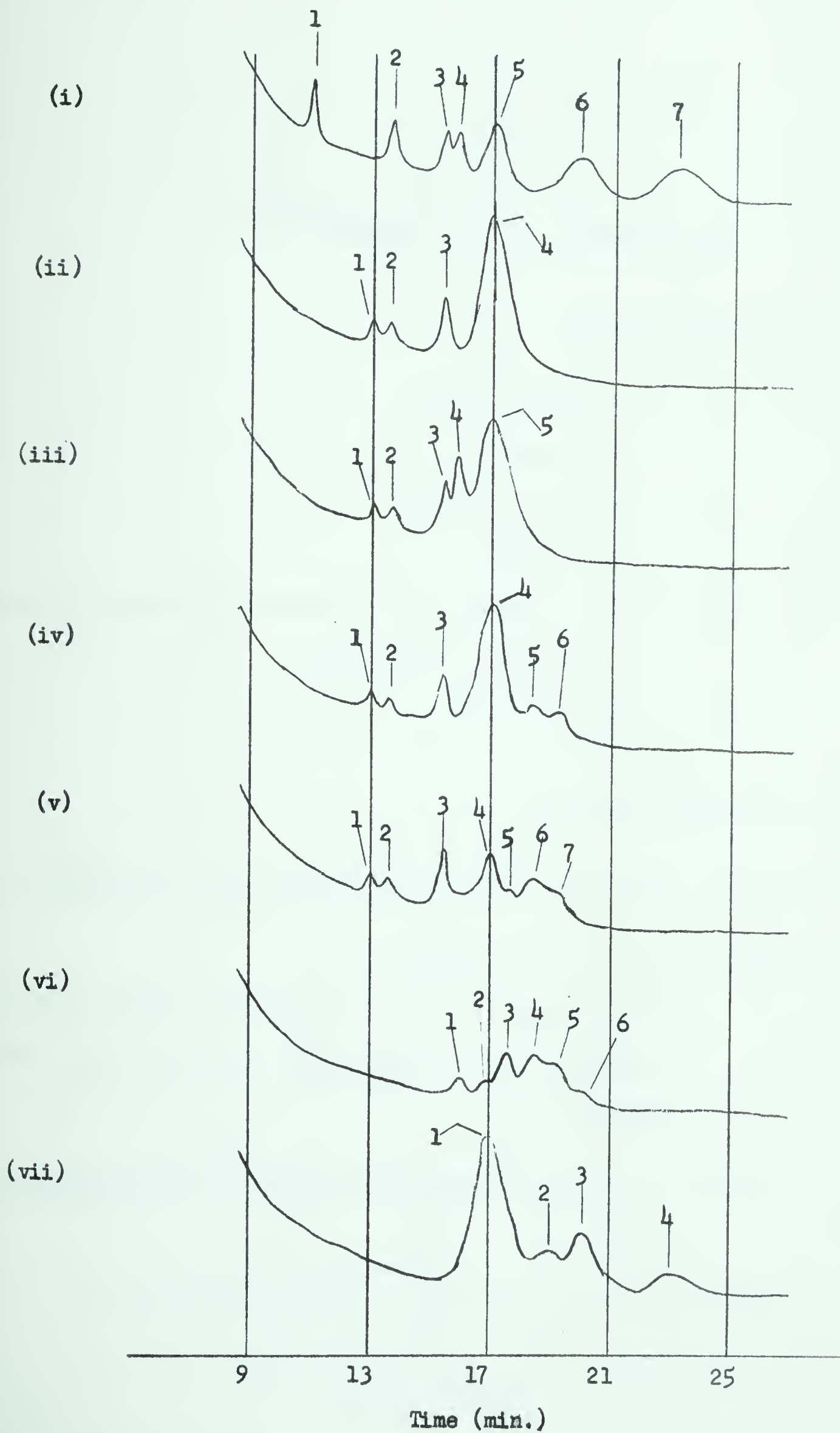


FIGURE II.12

V.P.C. Records - Silicone Rubber Column

(i) Authentic Compounds

1. n-decane, 1-decene
2. n-dodecane
3. Dicyclohexadiene
4. Dicyclohexyl
5. 2,2'-Dicyclohexenyl prepared cyclohexylcyclohexene,  
and phenyl cyclohexane
6. n-tetradecane

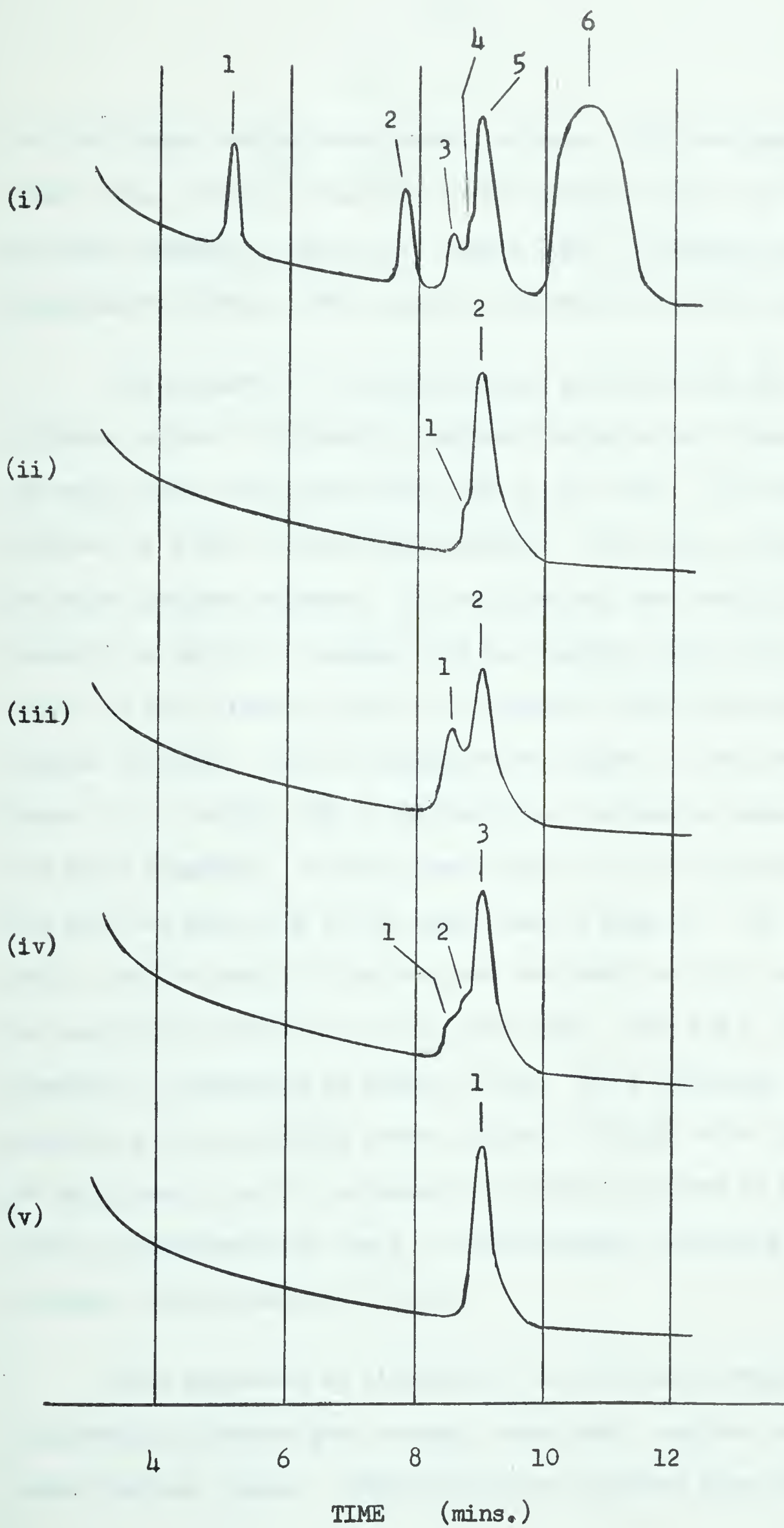
(ii) Irradiated cyclohexene

(iii) Irradiated solution of 0.2% 1,3-cyclohexadiene in cyclohexene

(iv) Prepared cyclohexyl cyclohexene.

(Preparation by dehydration of 4-cyclohexenyl cyclohexanol  
by dehydration of 2-cyclohexyl cyclohexanol gave Peak 3 as  
main peak).

(v) Irradiated pure 1,4-cyclohexadiene and product from preparation P<sub>2</sub> .







both silica-gel and silicone rubber columns. Its mass spectrum (Table II.4, Column 1) was in general agreement with that published for this compound in the A.P.I. manual (88). Analysis by N.M.R. spectrometry (Varian A-60) showed no aromatic or olefinic protons.

The prepared 2,2'-dicyclohexenyl gave one peak only from silicone rubber. Silica-gel separated one major and three minor peaks, the major peak area representing 92% of the total. The material was analyzed by N.M.R. and mass spectrometry. Table II.4, column 2, gives the mass spectrum obtained. No mass spectral data are given for this material in the A.P.I. manual, but the spectrum given for 1,5-hexadiene, which can also cleave to give two identical allylic radicals, shows similar features. For 1,5-hexadiene the height of the parent peak (mass 82), is only 1.31% of the height of the mass 41 peak, which is the major fragment. It can be seen that for 2,2'-dicyclohexenyl the mass 162 peak was only 0.3% of the major peak of mass 81. Due to its very small size the mass 162 peak was not observable at 11 V, so it could not be positively identified as the parent peak. The N.M.R. (Varian HR-100) spectrum is reproduced in Figure II.13A. The integration of this spectrum gave an olefinic proton content of 21.6% (after correction for 2% dicyclohexyl and 2% cyclohexylcyclohexene, present as impurities). This is consistent with the 2,2'-dicyclohexenyl structure (22.2% olefinic protons), within analytical error.

When separated by silica-gel, the materials prepared as isomers of cyclohexylcyclohexene gave a single main peak, together with several minor, rather diffuse, peaks. Triple peaks were obtained from silicone rubber



TABLE II.4

Mass Spectral Data - I

Column (1)	Aldrich dicyclohexyl (Peaks < 1% of major peak not included).
Column (2)	Prepared 2,2'-dicyclohexenyl (Peaks < 2% of major peak not included for m/e < 140).
Column (3)	Prepared cyclohexylcyclohexene (Peaks < 10% of major peak not included).
Column (4)	Dimers from irradiated cyclohexene (Peaks < 1% of major peak not included).
Column (5)	Dimers from preparation P <sub>2</sub> (Peaks < 3% of major peak not included for m/e < 95).

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>(5)</u>
27	10.5	7.7	26.8	20	10
28	12.0	3.0	11.8	28	12
29	12.0	6.1	19.2	9	8
39	13.8	9.8	39.8	31	12
40	2.5	-	-	-	-
41	42.0	19.3	66.0	51	23
42	5.8	-	-	-	-
43	11.3	-	16.2	-	-
44	3.7	-	-	-	-
51	-	2.2	-	7	7
52	-	-	-	-	4
53	6.9	11.1	22.3	20	14
54	15.0	2.3	21.6	38	8



TABLE II.4 (Continued)

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>(5)</u>
55	75.0	7.7	49.5	60	8
56	9.0	3.7	15.4	4	3
57	-	25.0	-	-	28
59	-	9.2	-	-	-
65	-	3.7	13.3	8	5
66	-	2.1	-	-	-
67	57.2	4.2	<u>100</u>	81	16
68	6.3	-	19.3	6	-
69	7.0	-	16.6	3	-
73	-	-	-	-	20
77	2.8	7.6	22.8	11	19
78	-	2.9	-	-	11
79	4.6	24.8	46.0	36	61
80	1.8	46.4	16.4	46	51
81	13.0	<u>100</u>	73.5	<u>100</u>	<u>100</u>
82	<u>100</u>	9.6	44.4	98	20
83	63.6	3.1	22.3	45	3
84	6.3	-	-	-	-
91	1.3	4.0	24.5	8	9
92	-	-	-	3	-
93	-	-	48.5	3	-
94	-	-	14.9	4	-
95	3.8	-	29.8	4	-
96	5.4	-	12.4	4	-
97	2.6	-	-	-	1





TABLE II.4 (Continued)

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>(5)</u>
98	-	-	-	-	2
100	-	3.3	-	-	3
103	-	-	-	-	2
104	-	-	-	-	2
105	-	-	10.0	-	1
107	-	-	33.6	-	-
108	-	-	23.1	-	-
109	3.5	-	13.8	-	-
115	-	-	-	-	5
116	-	-	-	-	1
117	-	-	-	-	2
121	-	-	29.2	-	-
122	-	-	11.8	-	-
128	-	-	-	-	3
129	-	-	-	-	6
130	-	-	-	-	5
131	-	-	-	-	1
135	-	-	13.8	-	-
141	-	1.3	-	-	2
143	-	-	-	-	3
149	-	-	38.8	-	-
152	-	-	-	-	1
153	-	-	-	-	1



TABLE II.4 (Continued)

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>	<u>(4)</u>	<u>(5)</u>
154	-	-	-	-	2
155	-	-	-	-	1
156	-	0.3	-	-	2
157	-	-	-	-	1
158	-	-	-	-	6
159	-	-	-	-	1
160	-	-	-	-	1
162	-	0.3	-	1	1
164	-	-	25	-	1
166	10.0	-	-	6	-
167	1.2	-	-	-	-

FIGURE II.13

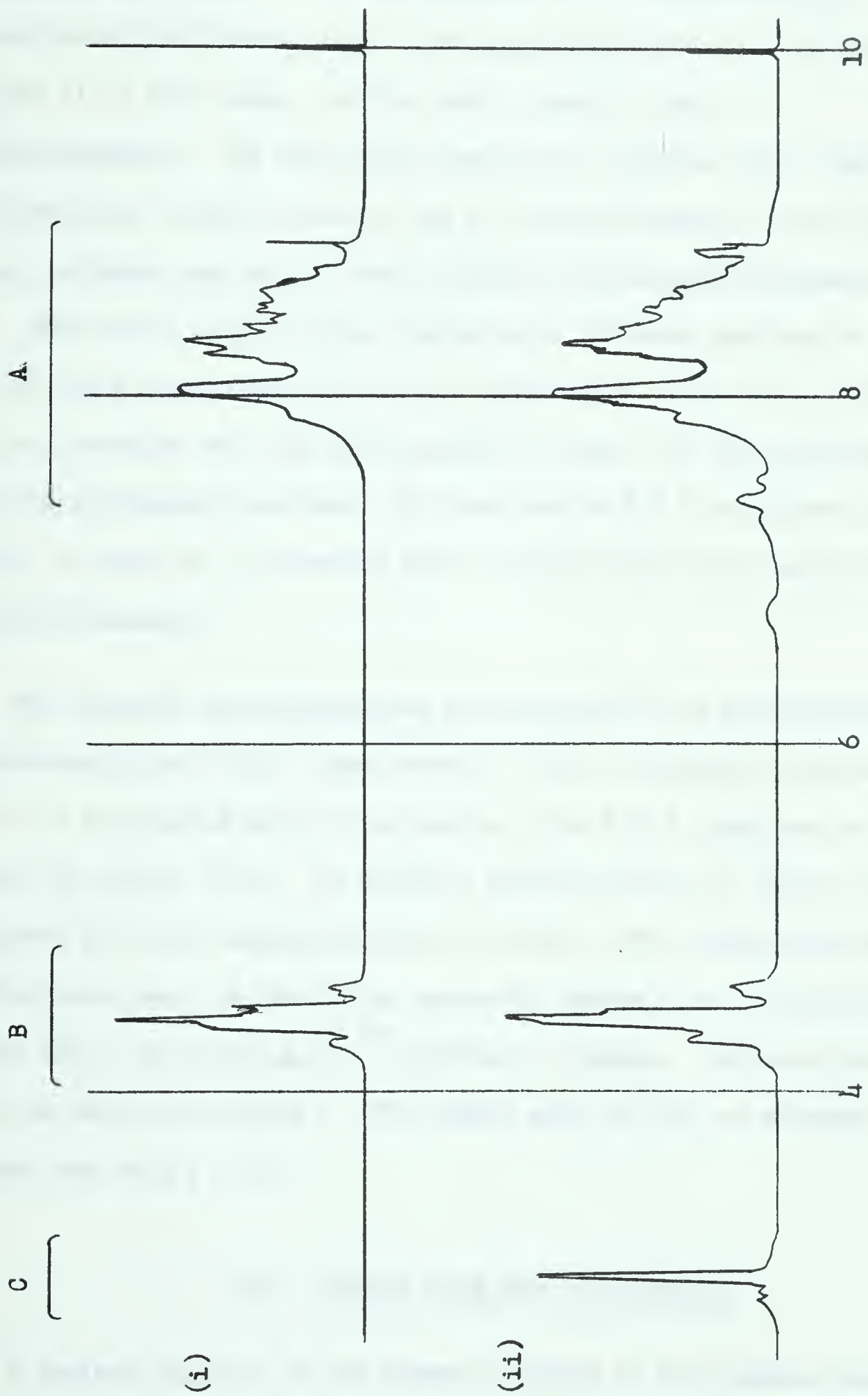
N.M.R. Spectra

- A Alkane type protons
- B Olefinic protons
- C Aromatic protons

(i) Prepared 2,2'-dicyclohexenyl

(ii) C<sub>12</sub>-hydrocarbons from preparation P<sub>2</sub>







(Figure II.12, line (iv) ), for the products of the dehydration of both 2-cyclohexylcyclohexanol and 4-cyclohexylcyclohexanol. The main peak (peak 3) in both cases, had the same retention time as 2,2'-dicyclohexenyl. The two smaller peaks had retention times that were intermediate between dodecane and 2,2'-dicyclohexenyl in both cases, which may indicate that one of the  $C_6$  rings of cyclohexylcyclohexene had opened. This could explain those fragments in the mass spectrum of the product of the 2-cyclohexylcyclohexanol dehydration (Table II.4, column 3), that do not coincide with the major peaks in either the dicyclohexyl or the 2,2'-dicyclohexenyl spectra. The spectrum at 8.8 V consisted of one peak only, of mass 164, indicating that the impurities were isomers of cyclohexylcyclohexene.

The prepared dicyclohexadiene was analyzed by uv spectrophotometry, mass spectrometry and N.M.R. spectrometry. The uv analysis indicated the absence of a conjugated double bond system. The N.M.R. spectrum is reproduced in Figure II.14. An olefinic proton content of 25% was observed, which agrees with the dicyclohexadiene structure. The unsymmetrical nature of the olefinic peaks in the N.M.R. spectrum, agrees with the expected structure (83), tricyclo $[4,4,2^{7,10},0]$ dodeca-2,8-diene. The mass spectrum is given in Table II.5, line 1. The parent mass is 160, as expected. The major peak has an  $m/e = 80$ .

### (iii) Dimers from Pure Cyclohexene

A typical analysis of the dimers produced in cyclohexene radiolysis, using a silica-gel column, is shown in Figure II.11, line (ii).

FIGURE II.14

N.M.R. Spectrum - Dicyclohexadiene

- A        Alkane type protons
- B        Olefinic protons

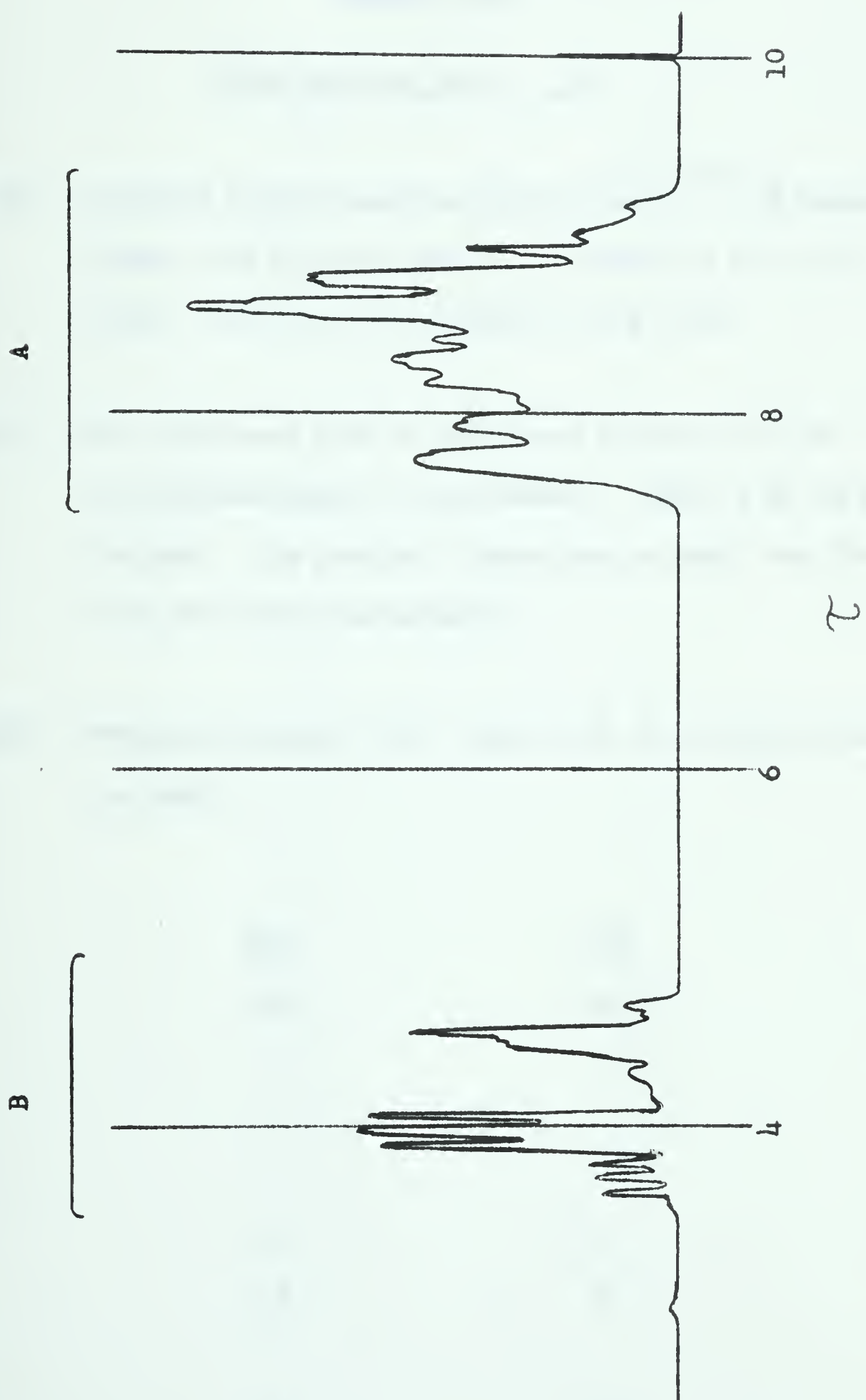






TABLE II.5

Mass Spectral Data - II

- Column (1) Prepared dicyclohexadiene (tricyclo [4,4,2<sup>7,10</sup>,0] dodeca-2,8-diene)  
(Peaks <1% of major peak not included for m/e <80 .  
Peaks <0.1% are not included for m/e >80).
- Column (2) D-5, separated from an irradiated solution of 0.6%  
1,3-cyclohexadiene in cyclohexane. (Peaks <1% are not  
included. The available sample was so small that the peaks  
<1% were barely detectable).
- Column (3) Phenylcyclohexane (88) (Peaks <3% of the major peak not  
included).

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>
27	3.9	14	27.2
28	-	-	7.9
29	-	-	13.1
38	-	-	3.3
39	5.7	17	26.6
41	3.5	22	21.5
50	-	-	7.4
51	3.3	9.3	17.2



TABLE II.5 (Continued)

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>
52	1.9	5	5.1
53	2.4	6	5.6
54	-	6	3.8
55	-	18	4.5
63	1.0	4	7.6
65	2.7	7	9.2
67	1.8	18	6.5
69	-	-	4.6
77	7.0	14	14.2
78	6.1	12	15.2
79	25.7	35	4.0
80	<u>100</u>	<u>100</u>	-
81	7.5	19	-
82	7.1	27	4.3
83	0.5	14	-
89	0.4	2	3.4
91	4.9	21	72.4
92	0.7	5	23.5
93	0.3	4	-
94	-	4	-
102	0.3	2	3.8
103	0.6	3	11.5





TABLE II.5 (Continued)

<u>m/e</u>	<u>(1)</u>	<u>(2)</u>	<u>(3)</u>
104	1.1	17	<u>100</u>
105	0.6	5	15.4
106	1.0	3	-
109	-	1	-
115	1.4	5	15.6
116	0.6	3	5.8
117	1.2	9	90.1
118	0.2	3	15.4
119	0.1	2	-
127	0.3	1	-
128	0.8	3	3.4
129	0.7	3	3.4
130	0.4	2	-
131	0.6	8	8.6
132	0.4	8	-
133	-	2	-
160	1.6 p	7 p	76.4 p
161	0.2	-	10.2

p - parent peak



Peak 1 has not been identified, but its retention time on silicone rubber was the same as that for the other three products, indicating that it too was probably a dimer. This product will be referred to as D-1 in later discussion. The compounds giving rise to peaks 2, 3 and 4 had the same retention times as dicyclohexyl, cyclohexylcyclohexene and 2,2'-dicyclohexenyl respectively, on both silica-gel and silicone rubber columns. Burns and Winter (80) identified a product having a yield similar to that of the product giving rise to peak 3, as 3-cyclohexyl cyclohexene. The silicone rubber analysis is shown in Figure II.12, line (ii). The shoulder (peak 1) was due to dicyclohexyl. The remaining dimers were eluted together (peak 2).

The four peaks were trapped together from silica-gel, and the 1  $\mu$ l of product obtained was analyzed by mass spectrometry. The spectrum obtained is given in column 4 of Table II.4. The fragmentation pattern was consistent with the identifications given. Two peaks only were observable in the region of mass 160, and these were barely detectable at 70 V. A satisfactory N.M.R. spectrum could not be obtained with the amount of product available.

(iv) Dimers from Solutions of 1,4-cyclohexadiene  
in Cyclohexene

Addition of 2% of 1,4-cyclohexadiene to cyclohexene gave rise to two new products, designated D-2 and D-3, in the analysis using silica-gel (Figure II.11, line (iv), peaks 5 and 6 respectively). All six dimers





were eluted simultaneously from the silicone rubber column with the same retention time as 2,2'-dicyclohexenyl (Figure II.12, line (v) ), indicating that all the products were probably dicyclic  $C_{12}$ -hydrocarbons.

Rajbenbach and Szwarc (89) have shown that the abstraction of  $\alpha$  hydrogen atoms by methyl radicals is relatively much faster from 1,4-cyclohexadiene than from cyclohexene. Since Ohnishi and Nitta (32) have identified 2-cyclohexenyl radicals in irradiated cyclohexene, and Fessenden and Schuler (31) have identified the dicyclohexadienyl radical in irradiated 1,4-cyclohexadiene, it might be expected that products arising from reactions involving cyclohexadienyl radicals would be observed in the radiolysis of the 1,4-cyclohexadiene/cyclohexene solutions, even for low diene concentrations. Thus it was concluded that cyclohexenylcyclohexadiene and dicyclohexadienyl\* were probable identities for the two new products D-2 and D-3, respectively. An attempt was therefore made to prepare these compounds in order to determine their retention times.

2,2'-dicyclohexenyl had been prepared in good yield when cyclohexene was heated with di-t-butyl peroxide (81). Therefore, the peroxide was heated with 1,4-cyclohexadiene to see if dicyclohexadienyl would be formed (preparation  $P_1$ ). Also, the peroxide was heated with 1,4-cyclohexadiene in excess cyclohexene (1 mole 1,4-cyclohexadiene: 3 moles di-t-butyl peroxide: 10 moles cyclohexene), in order to prepare a mixture of 2,2'-dicyclohexenyl, cyclohexenylcyclohexadiene and dicyclohexadienyl (preparation  $P_2$ ).

---

\* There are three isomeric compounds possible for dicyclohexadienyl, and two for cyclohexenylcyclohexadiene.





Seven products were obtained in the dimer fraction from preparation  $P_1$ , the highest yield being a product corresponding in retention time to biphenyl. Preparation  $P_2$  yielded four dimers that were distinguishable using the silica-gel column, as shown in Figure II.11 line (vii). Peaks 1 and 4 correspond to 2,2'-dicyclohexenyl and biphenyl respectively. Peak 2 apparently corresponds to peak 5 in both line (iv) (2% - 1,4-diene in cyclohexene) and line (vi) (pure 1,4-cyclohexadiene). Peak 3 may correspond to peak 6, line (vi) (pure 1,4-diene). All four compounds from preparation  $P_2$  and the dimers formed in the irradiation of all of the 1,4-diene/cyclohexene solutions, had the same retention time on silicone rubber, indicating that all were probably dicyclic  $C_{12}$ -hydrocarbons. (see Figure II.12, line (v) ).

The dimers produced by preparation  $P_2$  were analyzed by mass and N.M.R. spectrometry. The mass spectrum is given in Table II.4, column 5. It can be seen that while small peaks are present from mass 152 to 162 inclusive, most of the ion current was due to fragments. It was not therefore possible to characterize the components in the mixture, since parent peaks were not identifiable at low voltage. The N.M.R. spectrum is shown in Figure II.13B. Since the number of possible dicyclic  $C_{12}$ -hydrocarbons was large, the relative number of different types of proton could not give a guide to the compounds present. Integration of the spectrum showed a contribution due to aromatic protons of 6.5% . If peak 4 (biphenyl) were the only aromatic compound present, then only 3.6% of the spectrum should be due to aromatic protons. However, the adjacent peak 3 could not be entirely due to a phenyl substituted olefin, since in such a



case 11.1% of the spectra should be due to aromatic protons.

While the chemistry of the system suggests that the two new products formed due to the addition of 1,4-cyclohexadiene to cyclohexene (peaks 5 and 6 line (iv), Figure II.11) were probably due to isomers of cyclohexenylcyclohexene and isomers of dicyclohexadienyl, no positive identification was made, so they will be referred to as dimers D-2 and D-3 respectively.

The irradiation of pure 1,4-cyclohexadiene (line (vi) Figure II.11) gave rise to a product (peak 3), with a retention time on silica-gel similar to 2,2'-dicyclohexenyl. This product, which may be 3,3'-dicyclohexenyl, will be referred to as D-4.

(v) Dimers from Solutions of 1,3-cyclohexadiene  
in Cyclohexene

The V.P.C. records for the dimer analysis of an irradiated solution of 0.2% 1,3-cyclohexadiene in cyclohexene are given in Figure II.11, line (iii), and Figure II.12, line (iii), for silica-gel and silicone rubber columns respectively. A product is observed that was not present in the radiolysis of pure cyclohexene. (Peak 4, line (iii) Figure II.11 and peak 1, line (iii) Figure II.12). The retention times of this product are the same as those of the prepared dicyclohexadiene on both columns. Irradiation of 0.6% solution of 1,3-cyclohexadiene in cyclohexane also gave rise to a product that had retention times identical to those of the prepared dicyclohexadiene on these columns.



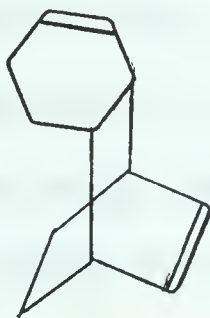




This product was not formed during the irradiation of pure cyclohexane.

The product formed in the irradiated cyclohexane solution was separated by V.P.C., collected and analyzed by mass spectrometry and uv spectrophotometry. The uv spectrum indicated an absence of a conjugated double bond system. The mass spectrum is given in Table II.5 column 2, where it can be compared with the spectra of the prepared dicyclohexadiene (column 1) and phenylcyclohexane (column 3). Some dicyclohexyl and cyclohexylcyclohexene were present in the irradiation product. There is a similarity between the spectrum of the radiolysis product and that of the prepared dicyclohexadiene, while the phenylcyclohexane spectrum is different from both.

The prepared dicyclohexadiene was the Diels-Alder adduct product of two 1,3-cyclohexadiene molecules, tricyclo[4,4,2<sup>7,10</sup>,0]dodeca-2,8-diene, shown below

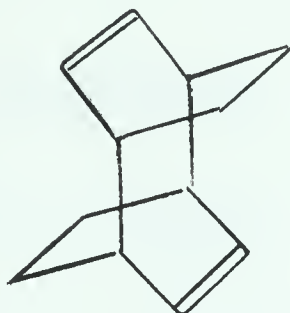


tricyclo[4,4,2<sup>7,10</sup>,0]dodeca-2,8-diene

The difference between the mass spectrum of the prepared material and the spectrum of the radiolysis product may be due to the presence of another isomer of dicyclohexadiene in the radiolysis products. For example the symmetrical adduct of two 1,3-cyclohexadiene molecules



may have been formed. Its structure is shown as follows



The observed radiolysis product will be referred to as dicyclohexadiene in future discussion.

(g) Appearance Potential Measurements

Appearance potentials were measured using a Metropolitan Vickers mass spectrometer, Type MS2. The compound being studied and Xenon, the reference material, were bled simultaneously into the ionization chamber throughout a determination. The pressures of both were adjusted initially so that the Xenon <sup>132</sup> peak, and the parent peak of the compound being studied, were approximately the same height when the electron voltage was 60 V .

To make the determination, the peak heights were measured as a function of the electron voltage, the voltage being varied in steps of 0.2 V. Readings were taken only as the peak height varied from approximately 6% to 0.1% of the height at 60 V. The results were calculated by the method described by Lossing et al, (90).



### SECTION III - RESULTS

#### (A) IRRADIATION OF PURE CYCLOHEXENE

##### (a) Major Products - Dose Dependence

Liquid cyclohexene was irradiated at a dose rate of  $\sim 9 \times 10^{18}$  ev/g hour. The major products measured were hydrogen ( $G_i = 1.28$ ), cyclohexane ( $G_i = 0.95$ ), 2,2'-dicyclohexenyl ( $G_i = 1.94$ ), dicyclohexyl ( $G_i = 0.23$ ), cyclohexylcyclohexene ( $G_i = 0.60$ ), an unidentified dimer, designated D-1 ( $G_i = 0.22$ ) and polymer ( $G_i = 2.3$ ). The yields of these products were studied as a function of dose. Extrapolation of the results to zero dose gave the initial G-values ( $G_i$ ) for these products (see Figure III.1). The values for  $G_i$  are summarized in Table III.1.

Because some products could be determined more accurately than others, the same range of dose was not used in all of the studies. Liquid products, except for polymer, were studied over the dose range  $4.94 - 21.2 \times 10^{19}$  ev/g. Polymer production was studied over the dose range  $26.0 - 103 \times 10^{19}$  ev/g. Hydrogen production was studied over the dose range  $0.252 - 22.1 \times 10^{19}$  ev/g.

No dose dependence was observed for the yields of hydrogen or cyclohexane. The results for hydrogen are presented in Table III.2 and Figure III.1B. The results for cyclohexane are presented in Table III.3 and Figure III.1A. The cyclohexane yields were obtained using the di-n-decyl phthalate column.



FIGURE III.1

Product Yields from Irradiated Cyclohexene - Dose Dependence

A

- Average total dimer
- ◇ 2,2'-Dicyclohexenyl
- Cyclohexane
- D-1

B

- Hydrogen
- 3-Cyclohexylcyclohexene
- Dicyclohexyl

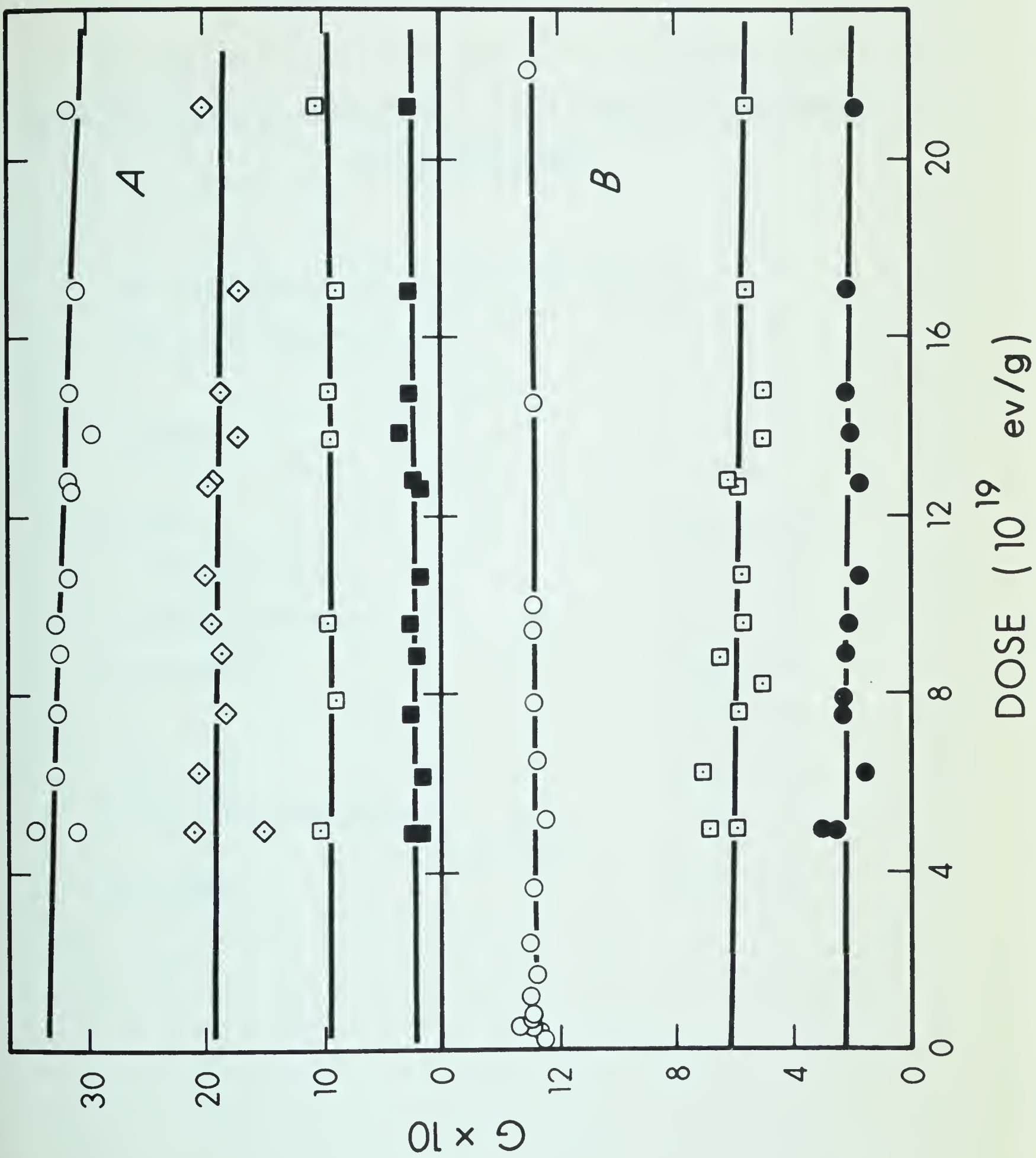




TABLE III.1

Initial G-values,  $G_i$ , of the Major Products Formed in the Irradiation  
of Pure Cyclohexene

Dose rate range =  $8.45 - 9.20 \times 10^{18}$  ev/g hour

Mean deviations are given.

<u>PRODUCT</u>	<u><math>G_i</math></u>
Hydrogen	$1.28 \pm 0.015$
2,2'-dicyclohexenyl	$1.94 \pm 0.13$
Cyclohexylcyclohexene	$0.60 \pm 0.05$
Dicyclohexyl	$0.23 \pm 0.03$
D-1	$0.22 \pm 0.04$
Total dimer	$3.35 \pm 0.30$
Polymer (excl. total dimer) in $C_6$ units	$2.3 \pm 0.8$
Cyclohexane	$0.95 \pm 0.05$

# 100

The following table shows the results of the 100 trials conducted on the 100 trials.

The following table shows the results of the 100 trials conducted on the 100 trials.

Trial	Result
1	100
2	100
3	100
4	100
5	100
6	100
7	100
8	100
9	100
10	100
11	100
12	100
13	100
14	100
15	100
16	100
17	100
18	100
19	100
20	100
21	100
22	100
23	100
24	100
25	100
26	100
27	100
28	100
29	100
30	100
31	100
32	100
33	100
34	100
35	100
36	100
37	100
38	100
39	100
40	100
41	100
42	100
43	100
44	100
45	100
46	100
47	100
48	100
49	100
50	100
51	100
52	100
53	100
54	100
55	100
56	100
57	100
58	100
59	100
60	100
61	100
62	100
63	100
64	100
65	100
66	100
67	100
68	100
69	100
70	100
71	100
72	100
73	100
74	100
75	100
76	100
77	100
78	100
79	100
80	100
81	100
82	100
83	100
84	100
85	100
86	100
87	100
88	100
89	100
90	100
91	100
92	100
93	100
94	100
95	100
96	100
97	100
98	100
99	100
100	100



TABLE III.2

Hydrogen Yields from Cyclohexene, as a Function of Dose

Dose rate range =  $8.8 - 9.2 \times 10^{18}$  ev/g hour.

<u>DOSE x 10<sup>-19</sup></u> <u>ev/g</u>	<u>G(Hydrogen)</u>
0.252	1.24
0.280	1.24
0.392	1.26
0.487	1.28
0.505	1.33
0.570	1.29
1.18	1.29
1.60	1.28
1.67	1.27
2.41	1.29
3.63	1.28
5.13	1.24
6.50	1.27
7.81	1.28
9.42	1.28
9.98	1.28
14.5	1.28
22.1	1.30



TABLE III.3

Cyclohexane Yields from Cyclohexene, as a Function of Dose

Dose rate range =  $8.45 - 8.60 \times 10^{18}$  ev/g hour.

<u>DOSE x <math>10^{-19}</math></u> <u>ev/g</u>	<u>G(Cyclohexane)</u>
4.94	1.03
7.90	0.90
9.60	0.95
13.8	0.92
14.7	0.93
17.1	0.88
21.2	1.06

# Table 1

Summary of the results of the experiments on the effect of the concentration of the solution on the rate of the reaction

The rate of the reaction was measured by the change in the concentration of the reactants or products over a given time interval

Concentration of the solution (M)	Rate of the reaction (M/s)
0.1	0.01
0.2	0.02
0.3	0.03
0.4	0.04
0.5	0.05
0.6	0.06
0.7	0.07
0.8	0.08
0.9	0.09
1.0	0.10

The yields of 2,2'-dicyclohexenyl, cyclohexylcyclohexene and dicyclohexyl, shown graphically in Figure III.1, appear to have decreased slightly with increasing dose. These results are given in Table III.4. Also given in Table III.4 and Figure III.1, are the G-values for the unidentified dimer D-1. The yield of this product was independent of dose.

The total dimer yield was determined in two ways. One value was obtained by summation of the individual dimer peaks separated by the silica-gel column. An independent measurement was obtained using the silicone rubber column. The two sets of values for G(total dimer) thus obtained did not agree, silicone rubber giving a higher value (see Table III.5). Since there was no basis for discriminating between these values, they were averaged. It is these average values that are plotted in Figure III.1A. A slight decrease in G(total dimer) with increasing dose was observed.

Polymer yields are presented in Table III.6 and Figure III.2. Because the method of polymer determination was not sufficiently accurate, it was not possible to draw any conclusion about dose dependence.

#### (b) Minor Products

Certain compounds that came under consideration as products or possible products are presented in Table III.7 with their estimated G-values. The dose used in each case is also listed.





TABLE III.4

Dimer Yields from Cyclohexene, as a Function of Dose (Silica-Gel Column)

Dose rate range =  $8.45 - 8.75 \times 10^{18}$  ev/g hour.

<u>DOSE x 10<sup>-19</sup></u> <u>ev/g</u>	<u>G(2,2'-Dicyclo-</u> <u>hexenyl)</u>	<u>G(Dicyclo-</u> <u>hexyl)</u>	<u>G(Cyclohexyl-</u> <u>cyclohexene)</u>	<u>G(D-1)</u>
4.94	1.50	0.26	0.59	0.25
4.95	2.10	0.30	0.68	0.17
6.20	2.05	0.15	0.71	0.16
7.57	1.83	0.23	0.59	0.24
8.90	1.87	0.23	0.65	0.20
9.60	1.95	0.21	0.57	0.25
10.6	1.99	0.17	0.57	0.16
12.6	1.98	0.17	0.59	0.13
12.8	1.93	0.17	0.61	0.20
13.8	1.70	0.20	0.50	0.32
14.8	1.95	0.22	0.50	0.23
17.1	1.69	0.22	0.56	0.24
21.2	2.00	0.19	0.56	0.24



TABLE III.5

Total Dimer Yields\* from Cyclohexene, as a Function of Dose

Dose rate range =  $8.45 - 8.75 \times 10^{18}$  ev/g hour.

DOSE $\times 10^{-19}$ ev/g	G(Total Dimer)		
	Silicone Rubber Column	Silica-Gel Column	Average
4.94	3.58	2.60	3.09
4.95	3.67	3.25	3.46
6.20	3.48	3.07	3.28
7.57	3.63	2.89	3.26
7.90	3.67		
8.90	3.49	2.95	3.22
9.60	3.61	2.96	3.28
10.5	3.36		
10.6	3.44	2.89	3.16
12.6	3.37	2.87	3.12
12.8	3.41	2.91	3.16
13.8	3.20	2.72	2.96
14.8	3.48	2.79	3.14
17.1	3.45	2.71	3.08
21.2	3.36	2.99	3.18

\* The unidentified product, D-1, is included in the totals.





TABLE III.6

Polymer Yields (Excluding Dimer) from Cyclohexene, as a Function of Dose

Dose rate =  $7.6 \times 10^{18}$  ev/g hour.

DOSE x $10^{-20}$ <u>ev/g</u>	G(Polymer) <u>                    </u>
2.60	2.5
5.98	1.4
6.50	4.1
8.20	1.6
10.3	2.0



TABLE III.7

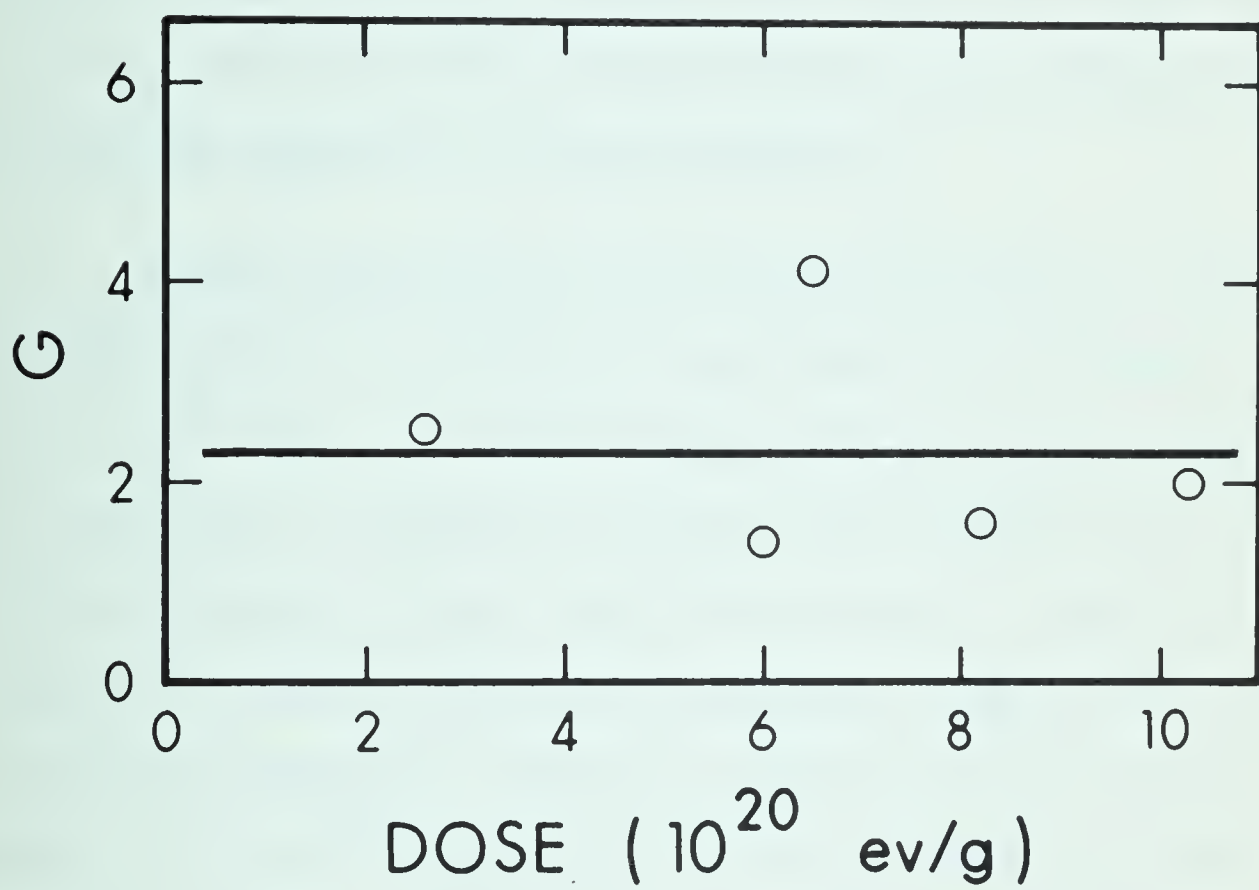
G-Values for Minor Products Formed in the Irradiation of Pure Cyclohexene

PRODUCT	G-VALUE	DOSE x 10 <sup>-19</sup> ev/g
1,4-cyclohexadiene	~0.05	73
1,3-cyclohexadiene	<0.10	23
Benzene	<0.05	23
1,5-hexadiene	~0.02	21.2
Unidentified C <sub>6</sub> -hydrocarbon	~0.03	21.2
Methane	~0.0013	38

FIGURE III.2

Polymer Yield from Cyclohexene

- Polymer, excluding dimers.







Benzene and 1,3-cyclohexadiene were not detected at the dose used, so the detection limits for these compounds using the 3,3'-oxydipropionitrile column, have been given.

1,4-cyclohexadiene was not detected in the dose dependence studies because of its small yield. At a dose of  $73 \times 10^{19}$  ev/g, a product, with the correct retention time on 3,3'-oxydipropionitrile for 1,4-cyclohexadiene, was just measurable.

Methane was detected in the product fraction not condensable at  $-196^{\circ}\text{C}$ , when a 2 ml sample of cyclohexene was irradiated to a dose of  $38 \times 10^{19}$  ev/g. It had not been possible to detect methane at the lower doses. Hydrogen and methane were separated using the activated charcoal column. Calibration factors for these two compounds, obtained under similar conditions by Myron (91), were used to estimate G(methane). Two minor products were detected at an absorbed dose of  $21.2 \times 10^{19}$  ev/g, using a di-n-decyl phthalate column. At lower doses the yields of these products had been too small to detect. The retention time for one was the same as that for 1,5-hexadiene. The second product is listed in Table III.7 as "unidentified  $\text{C}_6$  hydrocarbon". The retention time for this product, relative to cyclohexane and air, agreed with that given by DeMaré (92) for vinyl cyclobutane. Thus if vinyl cyclobutane was a product, its yield could not have been more than  $G = 0.03$ .

(c) Major Products - Dose Rate Dependence

The yields of hydrogen, cyclohexane, 2,2'-dicyclohexenyl,



cyclohexylcyclohexene and D-1, were measured as a function of dose rate, over the range  $1.32 - 265.0 \times 10^{17}$  ev/g hour. The results are given in Tables III.8, III.9 and III.10, and plotted in Figure III.3. No appreciable dose rate dependence was observed for any of these products, over the range studied.

Since the values for G(total dimer) obtained from the silica-gel and silicone rubber columns did not agree, they were averaged. The values and their averages are presented in Table III.11. The average values are plotted in Figure III.3. No dose rate dependence was observed for total dimer production.



TABLE III.8

Hydrogen Yields from Cyclohexene, as a Function of Dose Rate

$$\text{Dose} = 6.20 \times 10^{19} \text{ ev/g.}$$

<u>DOSE RATE x 10<sup>-18</sup></u> <u>ev/g hour</u>	<u>G(Hydrogen)</u>
1.33	1.28
2.80	1.24
2.89	1.25
3.56	1.26
5.52	1.27
11.0	1.24
19.1	1.29
31.8	1.29
88.1	1.25
242	1.28





TABLE III.9

Cyclohexane Yields from Cyclohexene, as a Function of Dose Rate

Dose range =  $1.22 - 1.38 \times 10^{20}$  ev/g.

DOSE RATE $\times 10^{-17}$ <u>ev/g hour</u>	<u>G(Cyclohexane)</u>
1.32	1.16
2.62	1.04
2.77	1.19
3.34	0.98
3.50	1.16
16.9	0.93
26.7	1.05
84.7	0.91
266	1.06



TABLE III.10

Dimer Yields from Cyclohexene, as a Function of Dose Rate (Silica-Gel Column)

Dose range =  $9.97 - 13.8 \times 10^{19}$  ev/g .

DOSE RATE $\times 10^{-17}$ ev/g hour	G(2,2'-Dicyclo- hexenyl)	G(Dicyclo- hexyl)	G(Cyclohexyl- cyclohexene)	G(D-1)
1.32	1.98	0.20	0.51	0.20
2.77	1.77	0.22	0.47	0.23
2.84	1.85	0.25	0.59	0.25
3.50	1.84	0.20	0.47	0.25
5.44	1.82	0.23	0.56	0.25
10.8	1.81	0.21	0.57	0.23
16.9	1.74	0.23	0.56	0.26
18.8	2.15	0.21	0.63	0.15
26.7	1.81	0.21	0.53	0.23
30.2	2.10	0.17	0.66	0.16
84.7	1.69	0.20	0.50	0.32
87.2	2.00	0.17	0.57	0.16
265	1.61	0.21	0.62	0.24

FIGURE III.3

Product Yields from Irradiated Cyclohexene - Dose  
Rate Dependence

A

- Average total dimer
- ◇ 2,2'-Dicyclohexenyl
- Cyclohexane
- D-1

B

- Hydrogen
- 3-Cyclohexylcyclohexene
- Dicyclohexyl

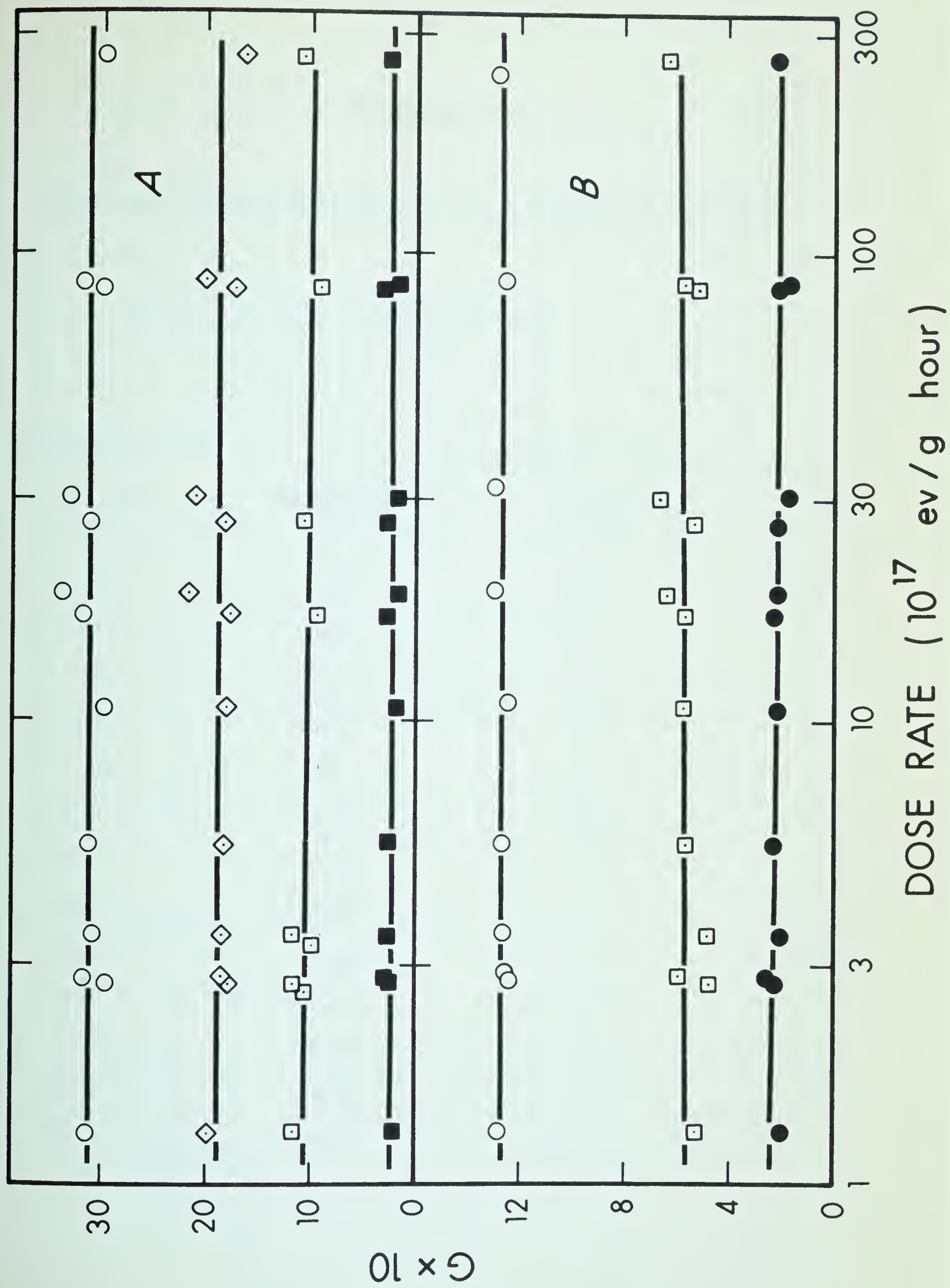






TABLE III.11

Total Dimer Yields from Cyclohexene, as a Function of Dose Rate

Dose range =  $9.97 - 13.8 \times 10^{19}$  ev/g .

DOSE RATE $\times 10^{-17}$ ev/g hour	G(Total Dimer)		
	Silicone Rubber Column	Silica-Gel Column	Average
1.32	3.35	2.89	3.12
2.77	3.17	2.69	2.93
2.84	3.40	2.94	3.17
3.50	3.36	2.76	3.06
5.44	3.36	2.86	3.11
10.8	3.10	2.82	2.96
16.9	3.54	2.78	3.16
18.8	3.56	3.14	3.35
26.7	3.38	2.78	3.08
30.2	3.46	3.09	3.28
84.7	3.20	2.72	2.96
87.2	3.44	2.90	3.17
265	3.26	2.68	2.97



(B) IRRADIATION OF CYCLOHEXENE WITH ADDITIVES

(a) Solutions Irradiated

Binary solutions of cyclohexene with added benzene, 1,3- and 1,4-cyclohexadiene were irradiated. Variations in the product yields were studied as a function of the electron fraction of additive,  $\epsilon_a$ . The electron fraction of additive is defined by

$$\epsilon_a = \frac{E_a W_a}{E_a W_a + E_c W_c}$$

where  $E_a$  and  $E_c$  give the number of moles of electrons per gram of additive and per gram of cyclohexene respectively.  $W_a$  and  $W_c$  are the respective weights of additive and cyclohexene in the mixture.

The additives varied widely in their effects on the various products. A comparison of these effects will now be given.

(b) Product Yields - Effect of Additives

(1) Hydrogen

G(hydrogen) values for the solutions of 1,4-cyclohexadiene in cyclohexene are given in Table III.12, for the benzene/cyclohexene solutions in Table III.13 and for the 1,3-cyclohexadiene/cyclohexene solutions in Table III.14. The results are compared graphically in Figure III.4. The broken lines in the Figure show the hydrogen yields that might have been expected if there had been no interaction between





the components, and if the energy absorption by each component in a solution were proportional to the electron fraction of that component. Thus the expected yield for hydrogen,  $G(H_2)_{ex}$  is defined by

$$G(H_2)_{ex} = G(H_2)_c^0 \epsilon_c + G(H_2)_a^0 \epsilon_a$$

where  $G(H_2)_c^0$  and  $G(H_2)_a^0$  are the hydrogen yields for pure cyclohexene and for pure additive, respectively, and  $\epsilon_c$  and  $\epsilon_a$  are the electron fractions for the respective components.

Inhibition is said to occur if the line obtained by plotting the observed G-values of a product, against the electron fraction of additive, falls below the line described by  $G_{ex}$  for that product, where  $G_{ex}$  for any product is defined in the same manner as  $G(H_2)_{ex}$  is defined above.

A low concentration of added 1,3-cyclohexadiene in cyclohexene caused a marked decrease in the hydrogen yield from the value of  $G = 1.28$ , obtained for pure cyclohexene. At high concentrations the rate of decrease became less marked and a value of  $G(H_2) = 0.235$  was obtained for pure 1,3-cyclohexadiene.

Benzene proved to be a less effective inhibitor than 1,3-cyclohexadiene at low concentrations. A value of  $G(H_2) = 0.038$  was obtained for pure benzene.

A value of  $G(H_2) = 1.19$  was obtained for pure 1,4-cyclohexadiene. The hydrogen yield decreased to this value when the electron fraction of





TABLE III.12

Hydrogen Yields from 1,4-Cyclohexadiene/Cyclohexene Solutions

Dose range =  $1.29 - 1.45 \times 10^{20}$  ev/g .

Dose rate =  $7.67 \times 10^{18}$  ev/g hour.

$\epsilon$  (Diene) = electron fraction of 1,4-cyclohexadiene.

$\epsilon$ (Diene)	0	0.0193	0.048	0.108	0.41	0.707	0.998
G(Hydrogen)	1.28	1.25	1.24	1.20	1.21	1.19	1.19

TABLE III.13

Hydrogen Yields from Benzene/Cyclohexene Solutions

Dose range =  $1.33 - 1.81 \times 10^{20}$  ev/g .

Dose rate =  $7.70 \times 10^{18}$  ev/g hour.

$\epsilon$  (Benzene) = electron fraction of benzene.

$\epsilon$ (Benzene)	0.013	0.051	0.096	0.206	0.407	0.715	1.00
G(Hydrogen)	1.24	1.15	1.04	0.816	0.525	0.247	0.038



TABLE III.14

Hydrogen Yields from 1,3-Cyclohexadiene/Cyclohexene Solutions

Dose range =  $1.34 - 1.37 \times 10^{20}$  ev/gm .

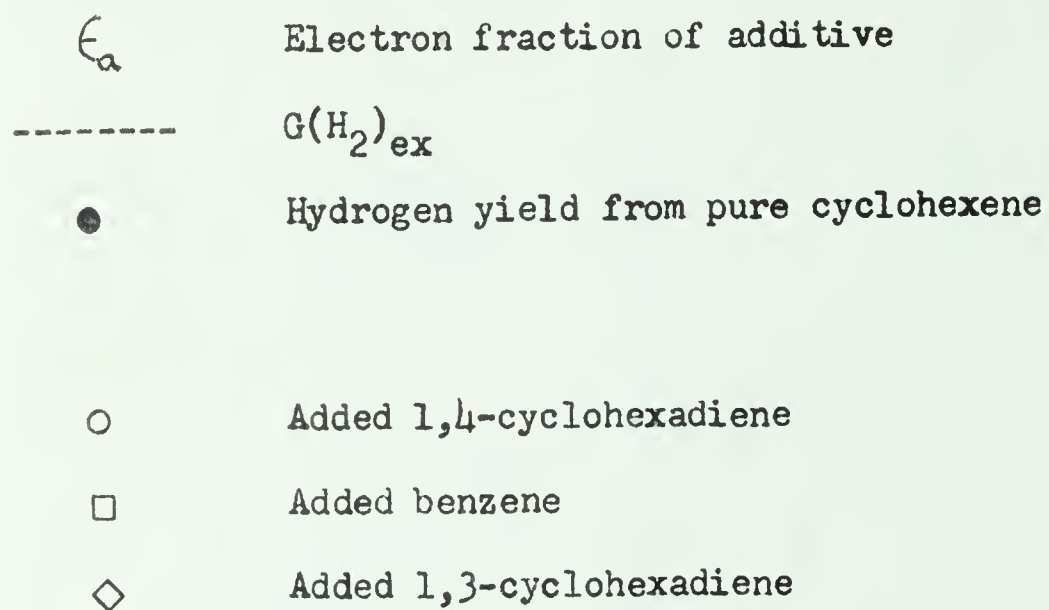
Dose rate =  $7.60 \times 10^{18}$  ev/g hour.

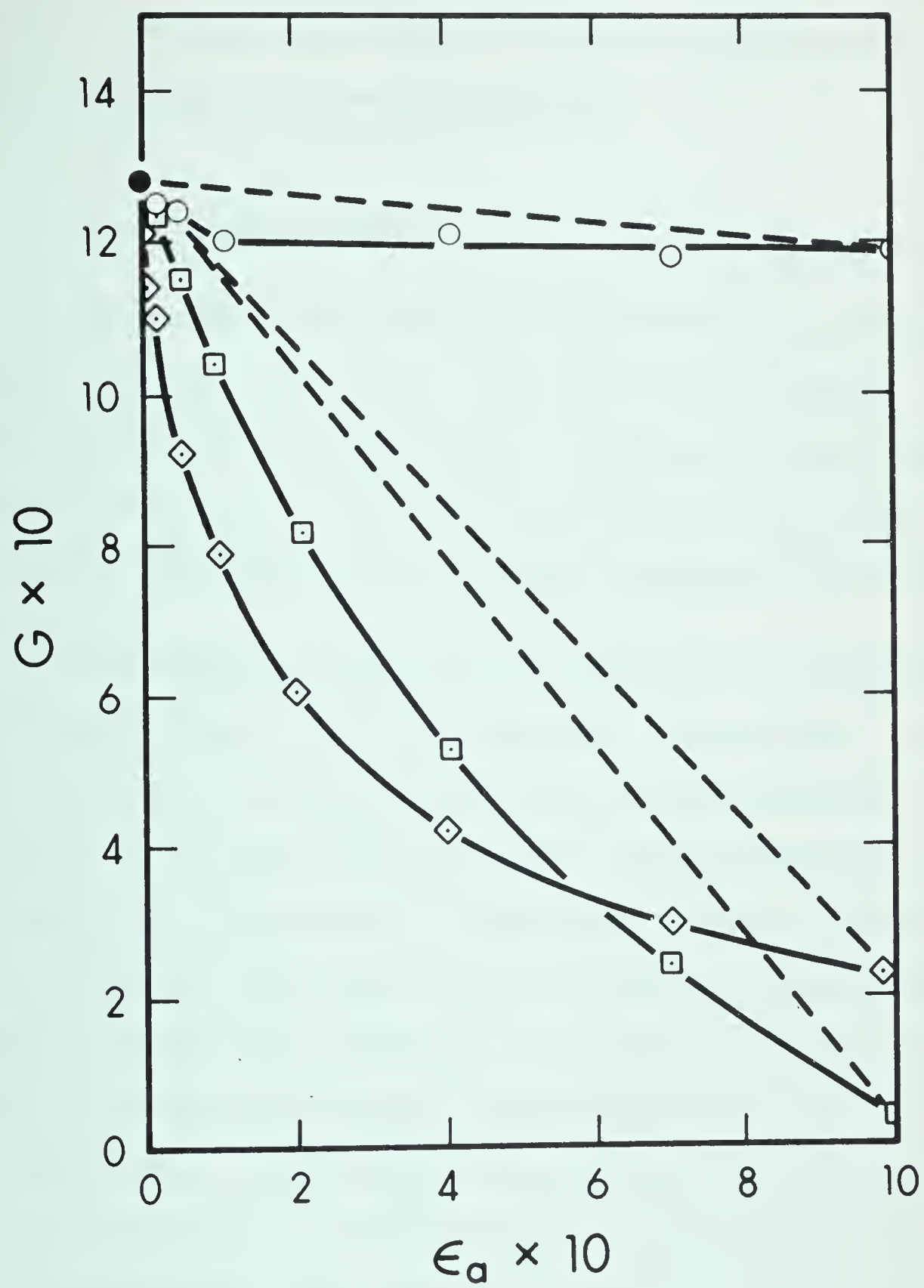
$\zeta_{(\text{Diene})}$  = electron fraction of 1,3-cyclohexadiene.

$\zeta_{(\text{Diene})}$	0	0.0033	0.0060	0.0192	0.048
G(Hydrogen)	1.28	1.21	1.14	1.10	0.93
$\zeta_{(\text{Diene})}$	0.096	0.195	0.398	0.702	0.989
G(Hydrogen)	0.79	0.61	0.42	0.30	0.236

FIGURE III.4

Hydrogen Yields - Cyclohexene Solutions









1,4-cyclohexadiene,  $\epsilon_{1,4\text{-diene}}$ , in the solution was increased to about 0.10 . The yield then remained constant as the electron fraction of 1,4-cyclohexadiene was increased.

## (2) Cyclohexane

G(cyclohexane) values for the 1,4-cyclohexadiene/cyclohexene solutions are given in Table II.15, for the benzene/cyclohexene solutions in Table III.16, and for the 1,3-cyclohexadiene/cyclohexene solutions in Table III.17. The results are compared graphically in Figure III.5. The broken line in the Figure represents  $G(\text{cyclohexene})_{\text{ex}}$ .

1,3-cyclohexadiene inhibited the production of cyclohexane even more effectively than it did that of hydrogen. G(cyclohexane) decreased from 0.95 to 0.14 as the electron fraction of 1,3-cyclohexadiene,  $\epsilon_{1,3\text{-diene}}$ , was increased from 0 to 0.097 . Benzene inhibited to a small degree only, having about the same effect on both the hydrogen and cyclohexene yields. Cyclohexane production from the 1,4-cyclohexadiene/cyclohexene solutions was approximately proportional to the electron fraction of the diene, with possibly some enhancement of the yield at low diene concentration. No cyclohexane was detected in the radiolysis of pure benzene or of pure 1,4-cyclohexadiene. No results were obtained for pure 1,3-cyclohexadiene radiolysis, due to its reactivity in the presence of air. However it can be seen from Figure III.5 that the yield of cyclohexane was tending to zero as  $\epsilon_{1,3\text{-diene}}$  approached 1.0 .



TABLE III.15

G-values from 1,4-Cyclohexadiene/Cyclohexene Solutions - C<sub>6</sub> HydrocarbonsDose rate range =  $7.95 - 8.25 \times 10^{18}$  ev/g hour.Dose range =  $14.0 - 15.6 \times 10^{19}$  ev/g . $\epsilon$  (Diene) = the electron fraction of 1,4-cyclohexadiene.

<u>PRODUCT</u>	$\epsilon$ (Diene)	0	0.0054	0.0196	0.103	0.301	0.558	0.998
Cyclohexane		0.95	0.99	0.95	0.91	0.71	0.40	0
1,3-Cyclohexadiene		0.10	0.18	0.13	0.51	0.60	0.77	0.56
Benzene		0.05						0.9
1,3-Cyclohexadiene + Cyclohexene								1.8
Cyclohexene (by difference)								1.2



TABLE III.16

G-values from Benzene/Cyclohexene Solutions

Dose rate =  $8.1 \times 10^{18}$  ev/g hour.

Dose range =  $1.40 - 2.22 \times 10^{20}$  ev/g .

$\epsilon$  (Benzene) = the electron fraction of benzene.

PRODUCT	$\epsilon$ (Benzene)	0	<u>0.021</u>	<u>0.052</u>	<u>0.106</u>	<u>0.213</u>	<u>0.413</u>	<u>0.662</u>	<u>1.00</u>
Cyclohexane		0.95	0.85	0.77	0.76	0.65	0.40	0.16	0
Dicyclohexyl		0.21	0.15	0.13	0.09	0.10	0.06	0.05	0
D-1		0.22	0.17	0.14	0.12	0.14	0.08	0.07	0
2,2'-Dicyclohexenyl		1.90	1.59	1.47	1.29	1.13	0.71	0.42	0
Cyclohexylcyclohexene		0.58	0.48	0.42	0.37	0.33	0.25	0.14	0
Total Dimer (Silica-Gel)		2.92	2.39	2.16	1.87	1.70	1.10	0.92	—
Total Dimer (Silicone Rubber)		3.46	2.78	2.97	2.94	2.23	1.73	1.20	0.14
Average Total Dimer		3.19	2.58	2.56	2.40	1.96	1.42	1.06	0.14





TABLE III.17

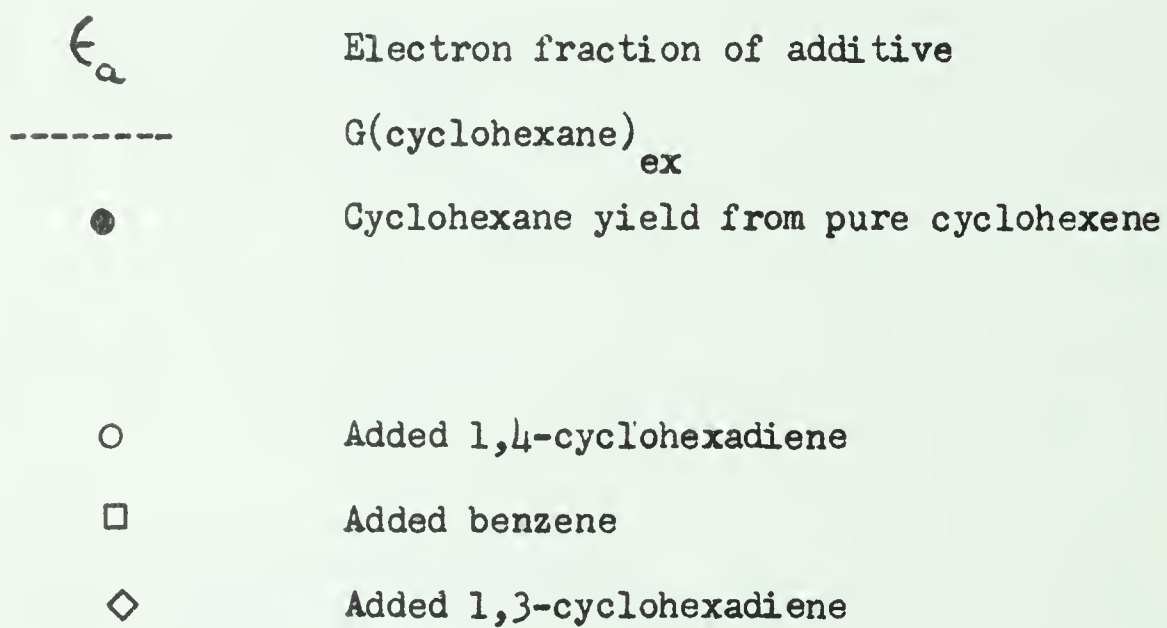
G-Values from the Irradiation of 1,3-Cyclohexadiene/Cyclohexene Solutions

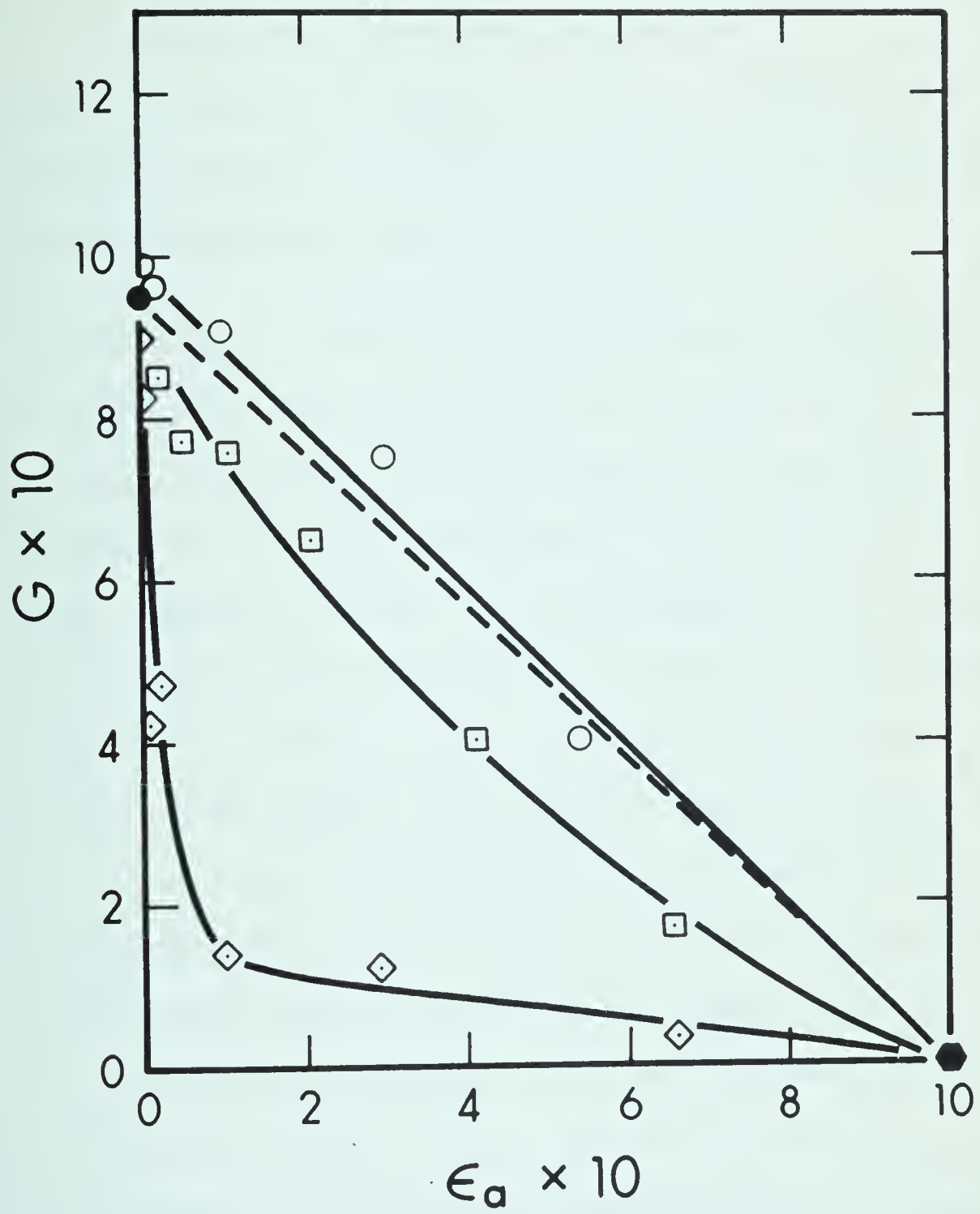
 $\zeta(\text{Diene})$  = Electron fraction of 1,3-cyclohexadieneDose rate =  $8.0 \times 10^{18}$  ev/g hour.      Dose range =  $1.35 - 2.16 \times 10^{20}$  ev/g.

PRODUCT	$\zeta(\text{Diene})$	0	0.0017	0.00202	0.0103	0.0202	0.097	0.292	0.66
Dicyclohexyl		0.21	0.15	0.18					
D-1		0.22	0.16						
2,2'-Dicyclohexenyl		1.90	1.60	1.46					
Cyclohexylcyclohexene		0.58	0.47	0.43					
Dicyclohexadiene		0	0.74	1.36	3.3	5.9	6.3	5.3	<4.0
Total Dimer (Silica-Gel)		2.92	3.12	3.27	4.58	6.68	6.10	6.85	
Total Dimer (Silicone Rubber)		3.46	4.15	4.64	6.0	8.3	8.9	6.5	6.3
Average Total Dimer		3.19	3.64	3.96	5.30	7.5	7.5	6.68	6.3
Cyclohexane		0.95	0.83	0.91	0.43	0.47	0.14	0.13	0.03
Benzene		<0.05	<0.05	<0.05	0.17	0.12	0.22	0.71	0.71
1,4-Cyclohexadiene		~0.05	~0	~0	~0	~0	~0	~0	~0

FIGURE III.5

Cyclohexane Yields - Cyclohexene Solutions







### (3) Dimers - Individual Yields

The G-values for the dimers produced from the 1,4-cyclohexadiene/cyclohexene solutions are given in Table III.18, from the benzene/cyclohexene solutions in Table III.16, and from the 1,3-cyclohexadiene/cyclohexene solutions in Table III.17.

The results for 2,2'-dicyclohexenyl, cyclohexylcyclohexene, dicyclohexyl and D-1 are presented graphically in Figures III.6, 7, 8 and 9 respectively. The broken lines represent  $G_{ex}$  in each case. 1,3-cyclohexadiene had the most marked effect on the production of these four compounds. Addition of 0.2% of 1,3-cyclohexadiene to pure cyclohexene reduced their yields by approximately 20% . The yield of dicyclohexadiene, a product which was not formed in pure cyclohexene, had increased to  $G \approx 1.4$  for such a 0.2% solution. For solutions where  $\epsilon_{1,3\text{-diene}}$  was more than 0.002 it was no longer possible to resolve and identify the individual dimers, using the silica-gel column. Dicyclohexadiene was separated from the other dimers by the silicone rubber column, however, for  $\epsilon_{1,3\text{-diene}}$  up to 0.29 . The yields for this product are shown in Figure III.10A, and it can be seen that the yield increase to a maximum of  $G = 6.3$  at  $\epsilon_{1,3\text{-diene}} \approx 0.05$  . The yield then decreased for higher concentrations of 1,3-cyclohexadiene, reaching a value of  $G = 5.3$  at  $\epsilon_{1,3\text{-diene}} = 0.29$  .

The combined yields of the dicyclic dimers are given in Figure 10.B. It can be seen that the curve must be a composite of the "cyclohexene type" dimers, which are decreasing with increasing 1,3-cyclohexadiene concentration,





TABLE III.18

G-Values from the Irradiation of 1,4-Cyclohexadiene/Cyclohexene Solutions - Dimers

$\zeta$  (Diene) = Electron fraction of 1,4-cyclohexadiene

Dose rate range =  $7.95 - 8.25 \times 10^{18}$  ev/g hour.      Dose range =  $1.40 - 1.56 \times 10^{20}$  ev/g .

PRODUCT	$\zeta$ (Diene)	0	0.0054	0.0196	0.103	0.301	0.558	0.998
Dicyclohexyl		0.21	0.16	0.14	0.095	0.060	0.025	0
D-1		0.22	0.18	0.13	0.07	0.03	0	0
2,2'-Dicyclohexenyl		1.90	1.53	1.13	1.75	0.50	0.52	0.33
D-4 (3,3'-Dicyclohexenyl?)								
Cyclohexylcyclohexene		0.58	0.53	0.47	0.40			
D-2(Cyclohexenylcyclohexadiene?)		0	0.30	0.33	0.44	0.38	0.48	0.35
D-3(Dicyclohexadienyl?)		0	0.22	0.33	0.39	0.43	0.55	<0.56
Biphenyl								0.05
Total Dimer (Silica-Gel)		2.92	2.87	2.50	2.20	1.82	1.93	1.45
Total Dimer (Silicone Rubber)		3.46	3.13	2.86	2.72	2.80	3.03	2.76
Average Total Dimer		3.19	3.00	2.68	2.46	2.31	2.48	2.1

FIGURE III.6

2,2'-Dicyclohexenyl Yields - Cyclohexene Solutions

$\epsilon_a$	Electron fraction of additive
-----	$G(2,2'\text{-dicyclohexenyl})_{ex}$
●	2,2'-Dicyclohexenyl yield from pure cyclohexene
○	Added 1,4-cyclohexadiene
□	Added benzene
◇	Added 1,3-cyclohexadiene

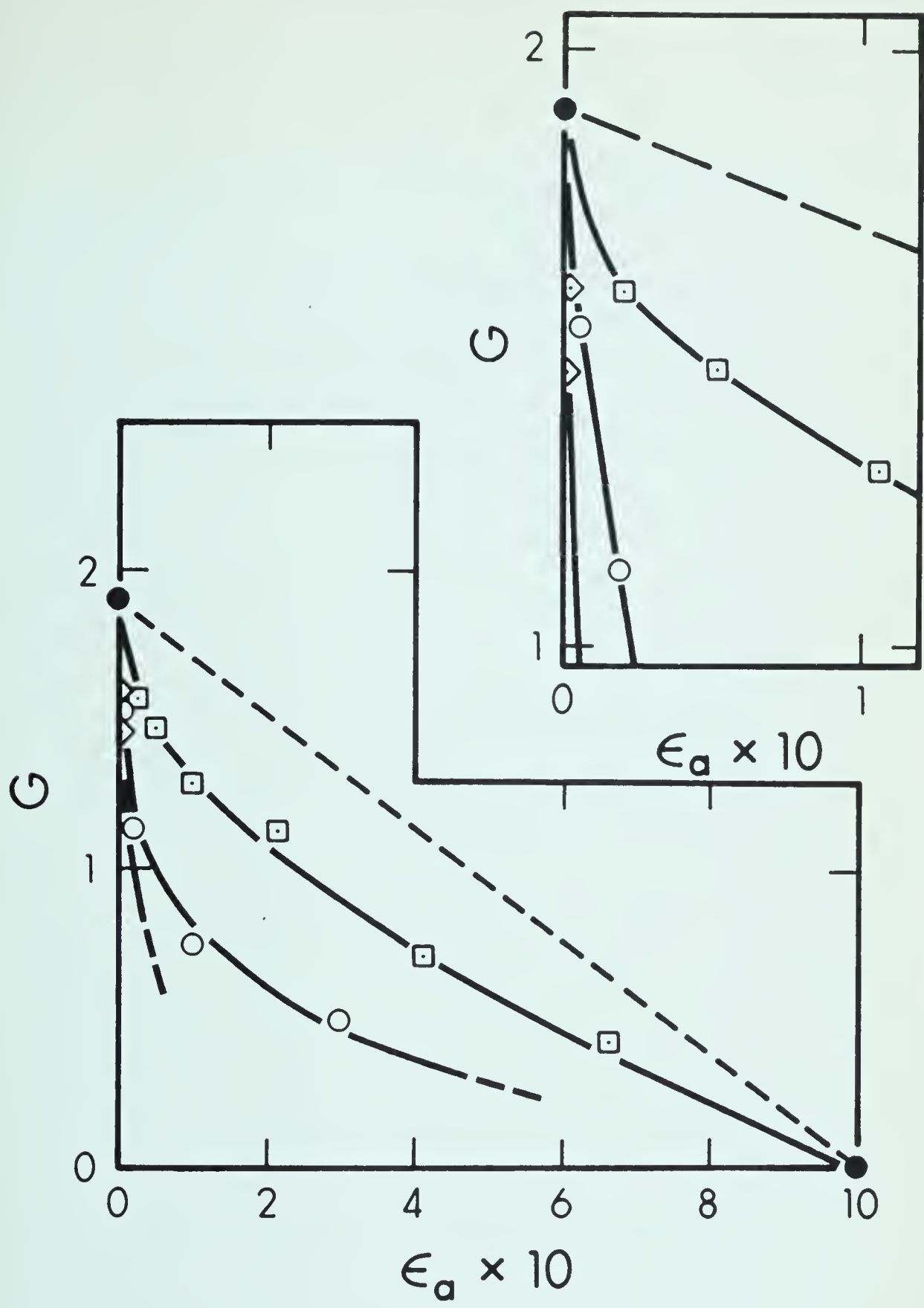
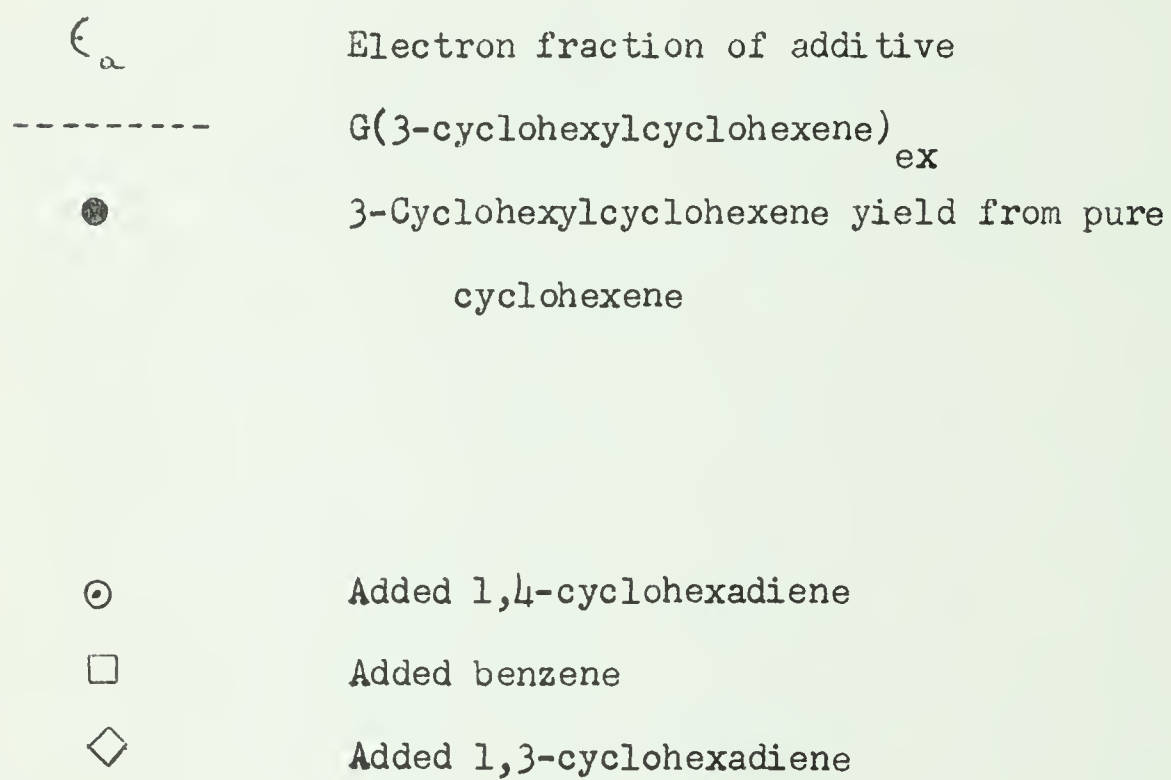


FIGURE III.7

3-Cyclohexylcyclohexene Yields - Cyclohexene Solutions



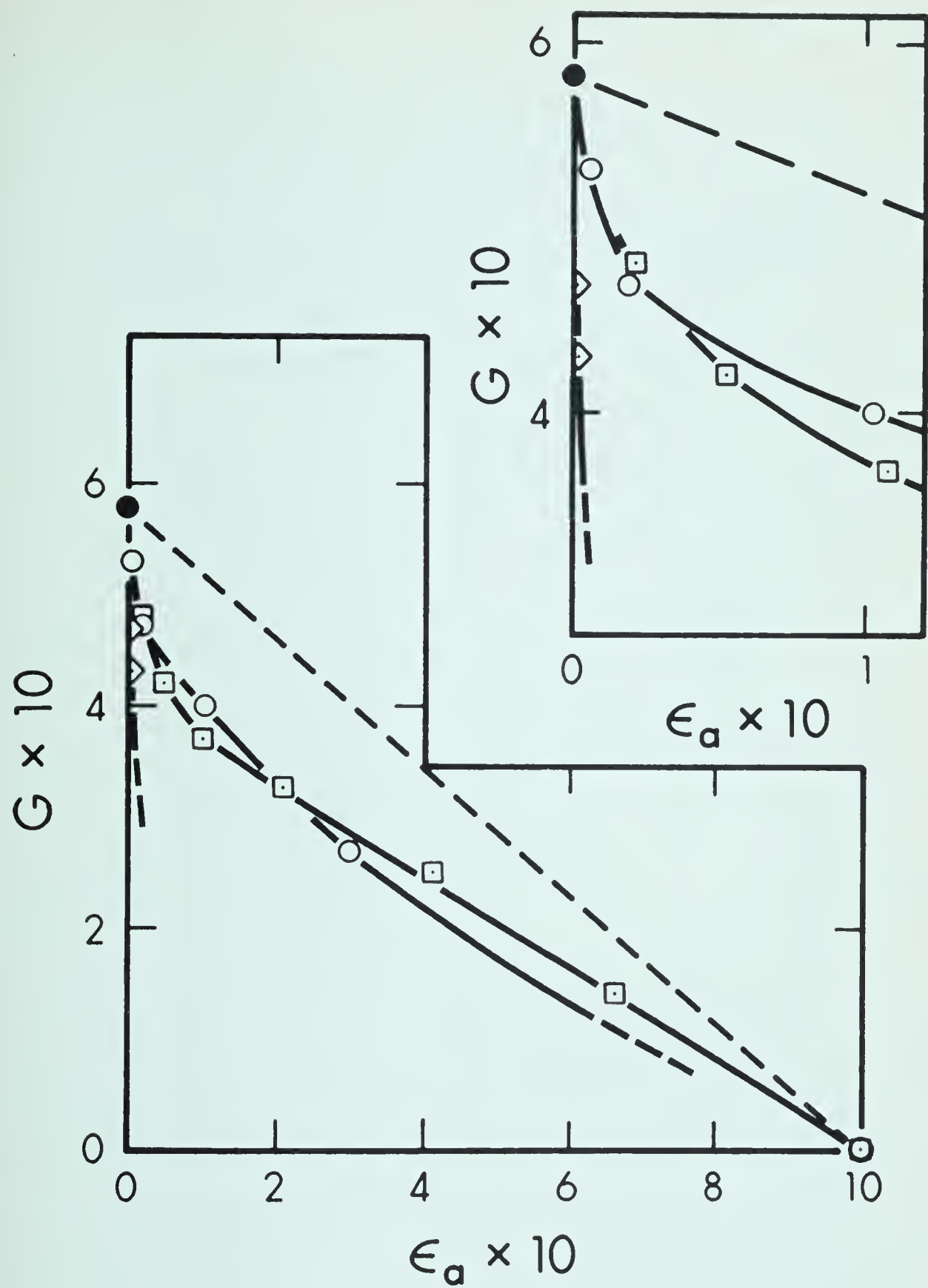




FIGURE III.8

Dicyclohexyl Yields - Cyclohexene Solutions

- $\epsilon_a$  Electron fraction of additive
- $G(\text{Dicyclohexyl})_{ex}$
- Dicyclohexyl yield from pure cyclohexene
- 
- Added 1,4-cyclohexadiene
- Added benzene
- ◇ Added 1,3-cyclohexadiene

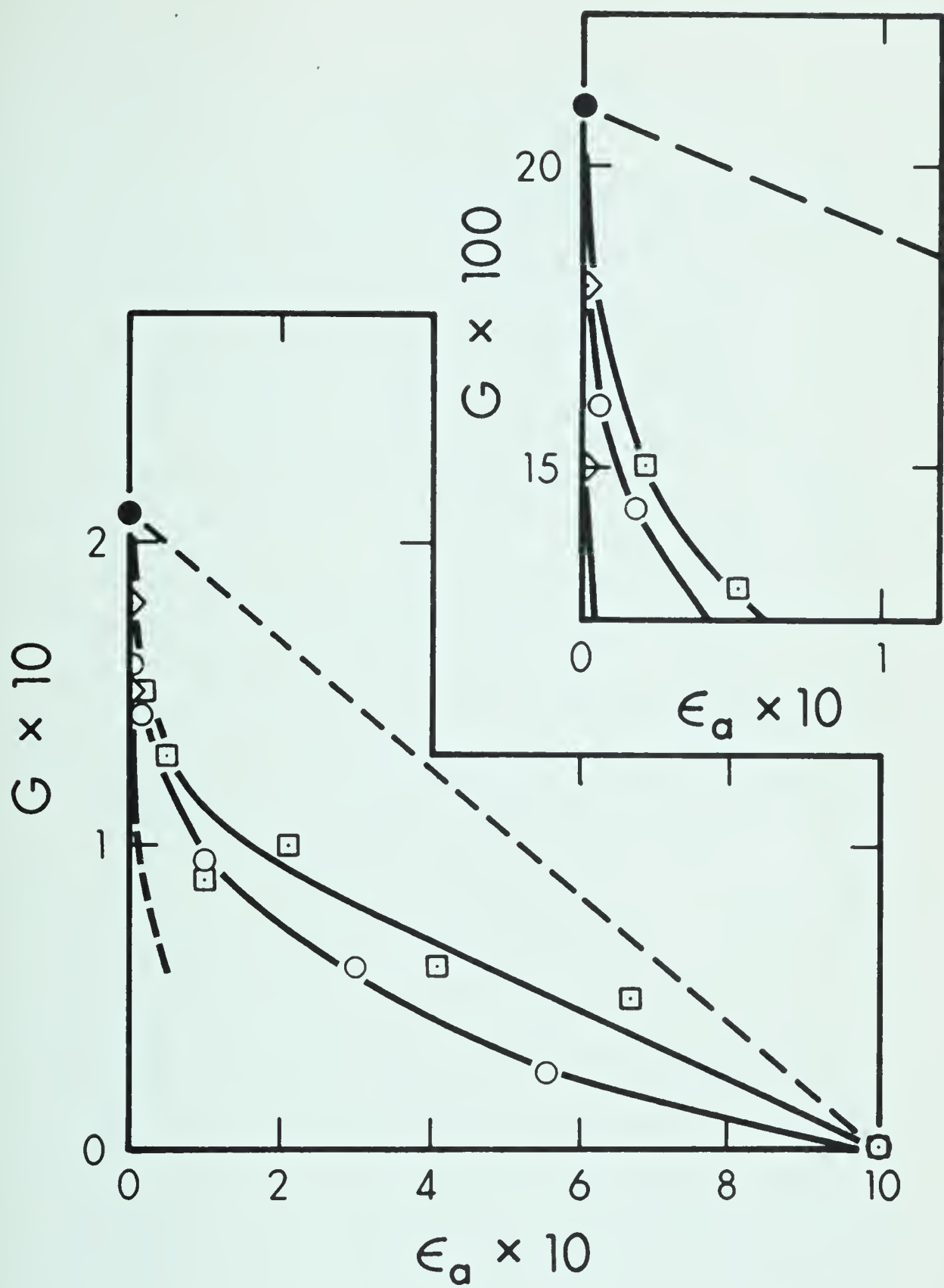
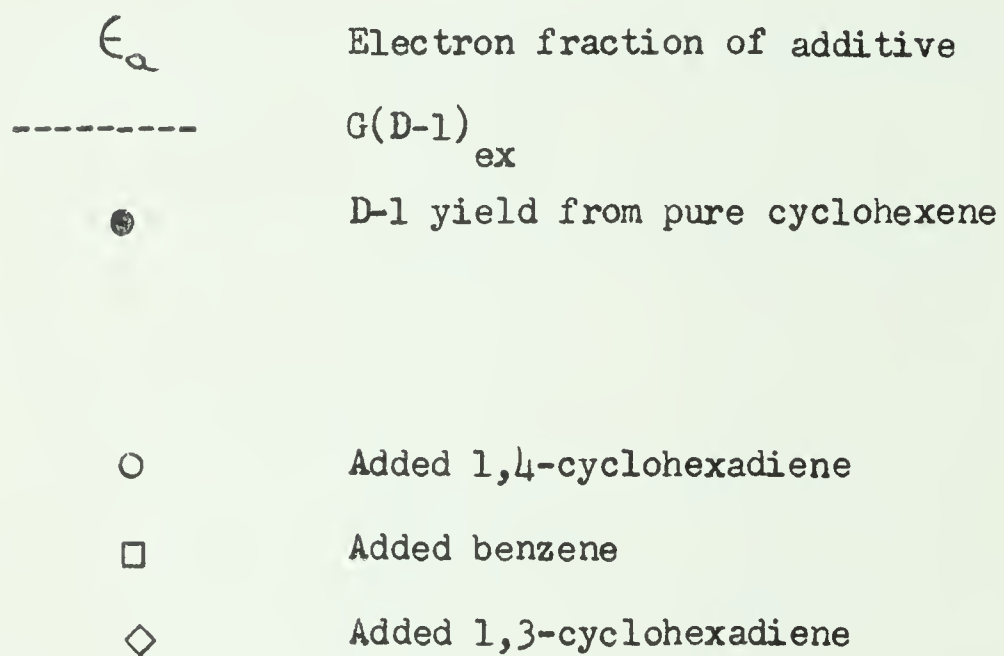


FIGURE III.9

D-1 Yields - Cyclohexene Solutions



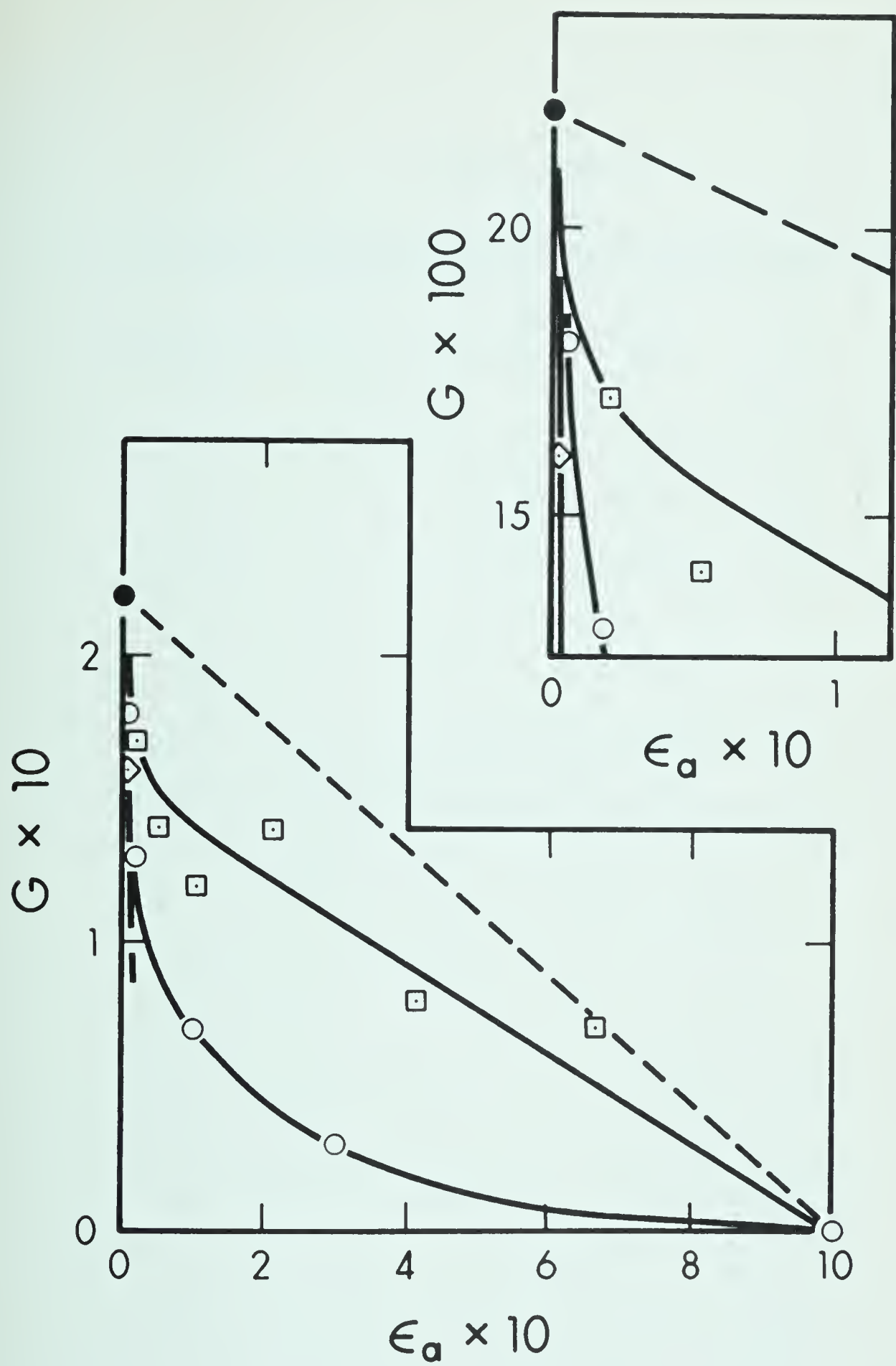


FIGURE III.10

Product Yields from 1,3-Cyclohexadiene/Cyclohexene Solutions

$\epsilon_a$  Electron fraction of 1,3-cyclohexadiene

A

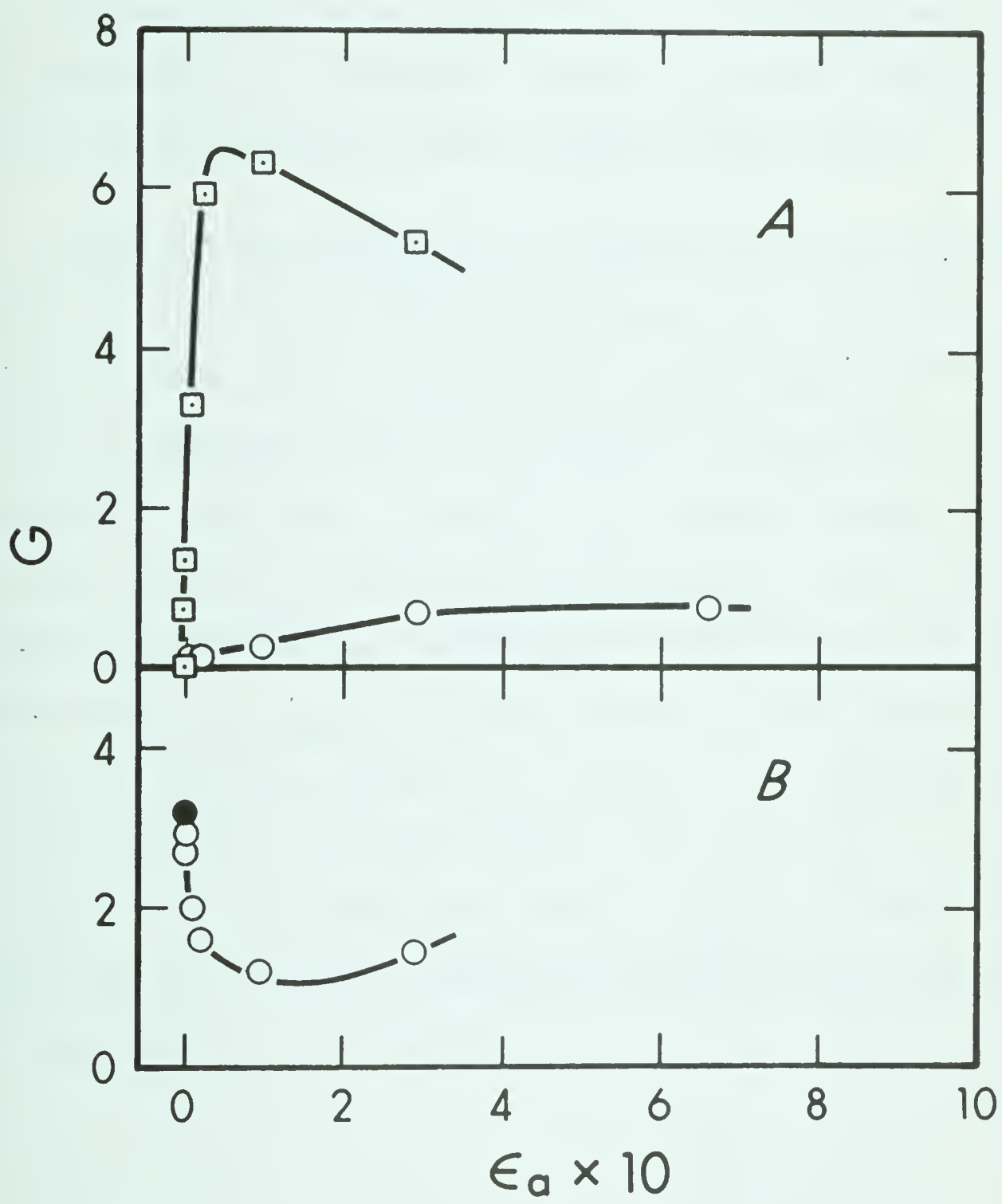
□ Dicyclohexadiene

○ Benzene yield

B

● Total dimer yield from pure cyclohexene

○ Total dicyclic dimer yield (i.e. Dimers that  
give dicyclohexyl on hydrogenation)







and dimers from the 1,3-cyclohexadiene system, which are increasing with increasing 1,3-cyclohexadiene concentration.

Benzene inhibited the production of 2,2'-dicyclohexenyl, cyclohexylcyclohexene, dicyclohexyl and D-1 to a small extent. The yields of these products decreased to zero for pure benzene.

Added 1,4-cyclohexadiene had approximately the same effect as benzene on the yields of cyclohexylcyclohexene and dicyclohexyl. The production of D-1 of 2,2'-dicyclohexenyl was inhibited more effectively. Two new  $C_{12}$ -hydrocarbon products, D-2 and D-3 (see page 86), not present in irradiated cyclohexene, appeared at low 1,4-cyclohexadiene concentration (see Figure III.11B). The yield of D-2, tentatively identified as cyclohexenylcyclohexadiene, increased to a maximum of  $G \approx 0.46$  for a solution with  $\epsilon_{1,4\text{-diene}} \approx 0.25$ , and then decreased to approximately  $G = 0.35$  for the pure 1,4-diene. The yield of D-3, tentatively identified as dicyclohexadienyl, increased rapidly to  $G = 0.4$  as  $\epsilon_{1,4\text{-diene}}$  was increased to 0.10, and gave a yield of  $G = 0.56$  for the pure 1,4-diene. Biphenyl was not produced in sufficient yield to be detectable using the silica-gel column. i.e.  $G < 0.05$ .

FIGURE III.11

Product Yields from 1,4-Cyclohexadiene/Cyclohexene Solutions

$\epsilon_a$  Electron fraction of 1,4-cyclohexadiene

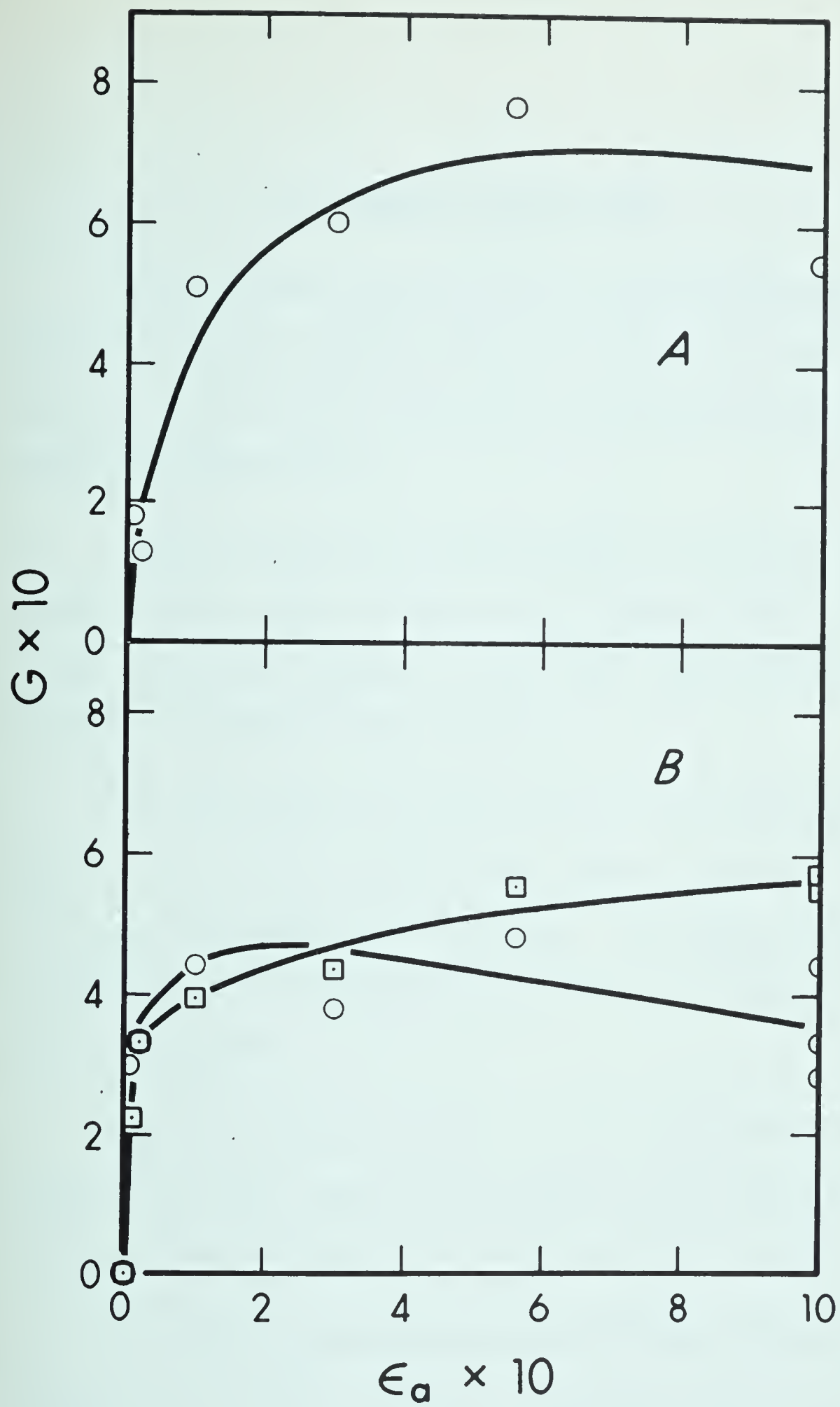
(A)

○ 1,3-cyclohexadiene

(B)

○ D-2 (cyclohexenylcyclohexadiene?)

□ D-3 (dicyclohexadienyl ?)





(4) Dimers - Total Yields

G(total dimer) values for the 1,4-cyclohexadiene/cyclohexene solutions are given in Table III.18, for the benzene/cyclohexene solutions in Table III.16 and for the 1,3-cyclohexadiene/cyclohexene solutions in Table III.17.

Since the values for G(total dimer), obtained using the silica-gel and the silicone rubber columns did not agree for any of the three solutions, the two values were averaged in every case. The average values for each solution are plotted in Figure III.12 .

The total dimer yield from the 1,4-cyclohexadiene/cyclohexene solutions was decreased by about 23%, from  $G = 3.19$  to  $G = 2.46$ , as  $\epsilon_{1,4\text{-diene}}$  was changed from 0 to 0.103 . For higher concentrations of the 1,4-diene the yield decreased only slightly, to a value of  $G = 2.1$  for pure 1,4-cyclohexadiene.

The total dimer production from the benzene/cyclohexene solutions followed the slight inhibition described for the individual dimers, since the total dimer yield from pure benzene is only  $G = 0.14$  .

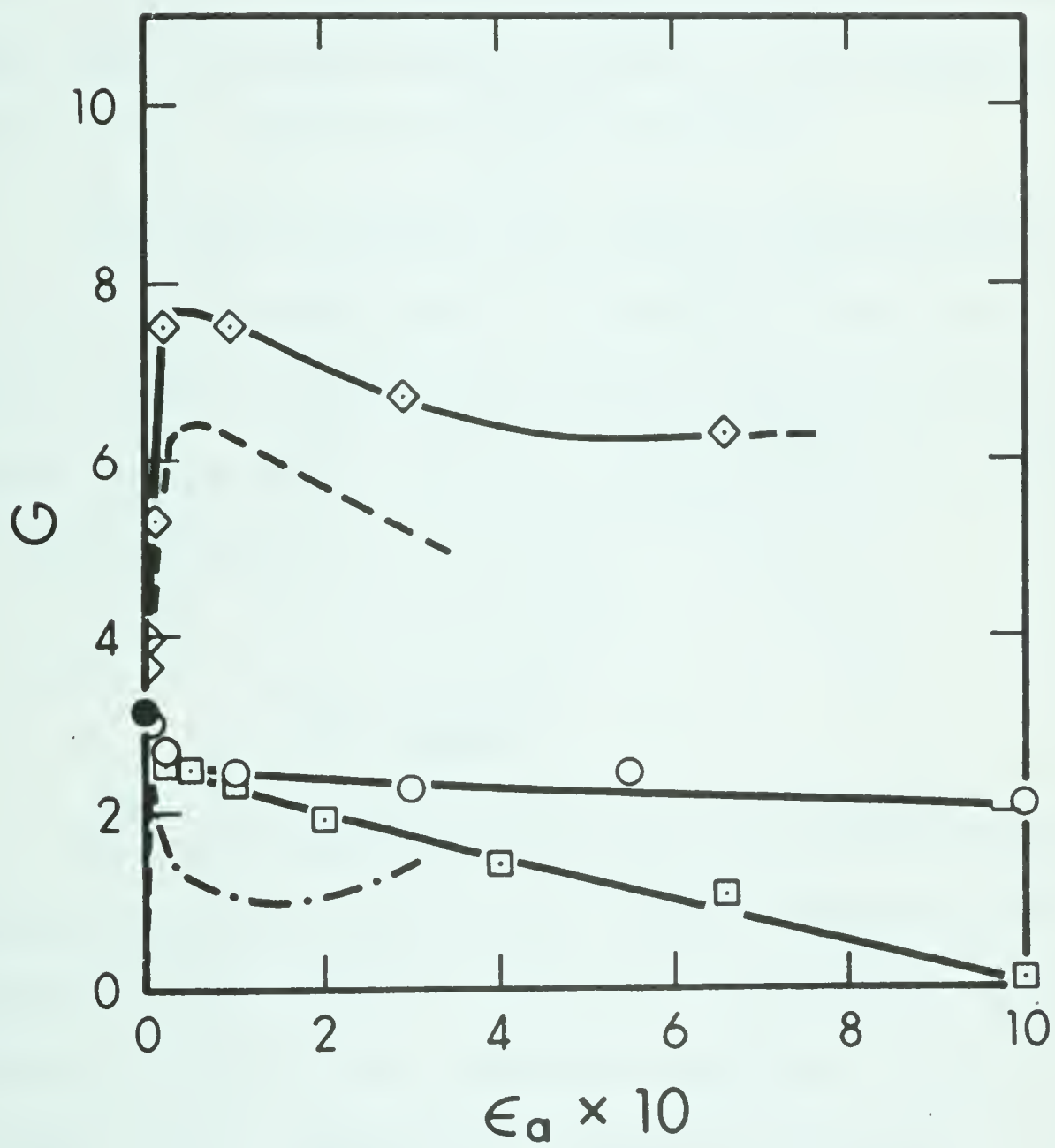
The total  $C_{12}$ -hydrocarbon yield increased from  $G = 3.19$  to a maximum of  $G \approx 7.5$  for a change of  $\epsilon_{1,3\text{-diene}}$  from 0 to 0.10 . The yield then decreased slowly to a value of  $G \approx 6.3$ , as the concentration of



FIGURE III.12

Total Dimer Yields - Cyclohexene Solutions

- $\epsilon_a$     Electron fraction of additive
- Total dimer yield from pure cyclohexene
- Added 1,4-cyclohexadiene
- Added benzene
- ◇    Added 1,3-cyclohexadiene
- Contribution of dicyclohexadiene to the total dimer  
yield from the 1,3-cyclohexadiene/cyclohexene solutions.
- - - - -    Contribution of other dimers to the total dimer yield  
from the 1,3-cyclohexadiene/cyclohexene solutions.





1,3-cyclohexadiene was further increased. The contribution of dicyclohexadiene to this yield is shown by the broken line in Figure III.12. No results were obtained for pure 1,3-cyclohexadiene because rapid and complex product formation in this material, in the presence of air, rendered the analysis valueless.

Total dimer production from a 10% 1,3-cyclohexadiene in cyclohexene solution was studied as a function of dose rate. The results are given in Table III.19 and the average values plotted in Figure III.13. A slight increase in  $G(\text{total dimer})$  with decreasing dose rate is observed.

#### (5) Polymer

The values for  $G(\text{polymer})$  from the 1,4-cyclohexadiene/cyclohexene solutions are given in Table III.20, from the benzene/cyclohexene solutions in Table III.21, and from the 1,3-cyclohexadiene/cyclohexene solutions in Table III.22. Yields from the three solutions are compared in Figure III.14.  $G(\text{polymer})$  from 1,4-cyclohexadiene was of the same order as that for cyclohexene. Benzene cause a reduction in polymer formation.

The method of analysis could not give an accurate determination of such low yields. Added 1,3-cyclohexadiene induced a rapid increase in the polymer yield, particularly at very low and very high concentrations.



TABLE III.19

Total Dimer Yield from a 1,3-Cyclohexadiene/Cyclohexene Solution,  
as a Function of Dose Rate

Electron fraction of 1,3-cyclohexadiene = 0.097 .

Dose range =  $1.59 - 1.72 \times 10^{20}$  ev/g .

DOSE RATE $\times 10^{-17}$ ev/g hour	G(Total Dimer)		
	Silicone Rubber Column	Silica-Gel Column	Average
238	8.52	7.30	7.91
75.2	8.39	7.31	7.85
3.13	9.25	8.85	9.05



FIGURE III.13

Total Dimer Yield from a 1,3-Cyclohexadiene/Cyclohexene  
Solution - Dose Rate Dependence

Electron fraction of 1,3-cyclohexadiene  
was 0.097 .

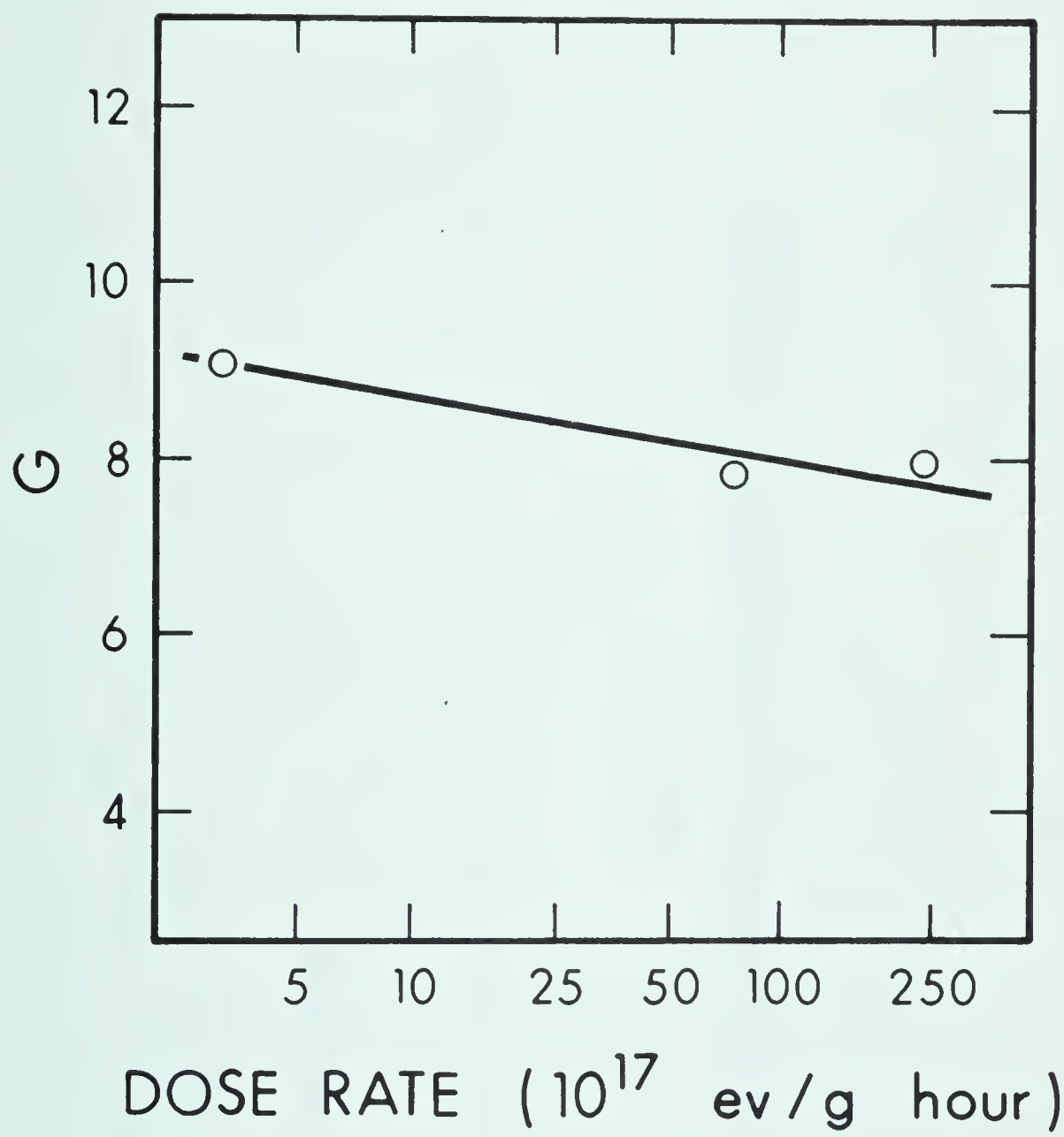




TABLE III.20

Polymer Yields (Excluding Dimers) from 1,4-Cyclohexadiene/Cyclohexene Solutions

Dose range =  $5.2 - 6.8 \times 10^{20}$  ev/g .

Dose rate = 7.6 ev/g hour.

Electron fraction of 1,4-cyclohexadiene	0	0.05	0.20	0.56	1.0
G(polymer)	2.3	4.7	2.83	3.15	4.1

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TABLE III.21

Polymer Yields (Excluding Dimers) from Benzene/Cyclohexene Solutions

Dose range =  $4.4 - 5.3 \times 10^{20}$  ev/g .

Dose rate =  $7.6 \times 10^{18}$  ev/g hour.

Electron fraction of benzene	0	0.05	0.20	0.56	1.0
G(polymer)	2.3	1.9	1.1	1.9	0.46



TABLE III.22

Polymer Yield (Excluding Dimer) from 1,3-Cyclohexadiene/Cyclohexene Solutions

Dose range =  $4.63 - 4.85 \times 10^{20}$  ev/g .

Dose rate =  $7.6 \times 10^{18}$  ev/g hour.

Electron fraction of 1,3-cyclohexadiene	0	0.045	0.18	0.49	0.89
G(polymer)*	2.3	9.7	14.0	23.6	40.7
		(8.1)	(11.7)	(19.7)	(34.0)

\* Analysis of the residue of the 89% 1,3-cyclohexadiene, 11% cyclohexene solution gave a composition of  $(C_6H_8O)_n$  with an average value of  $n = 8.7$  . If the oxygen addition took place before the determination of G(polymer), and it is assumed that oxygen addition took place in all the above solutions to the same extent, then the values for G(polymer) will be those given in parentheses.



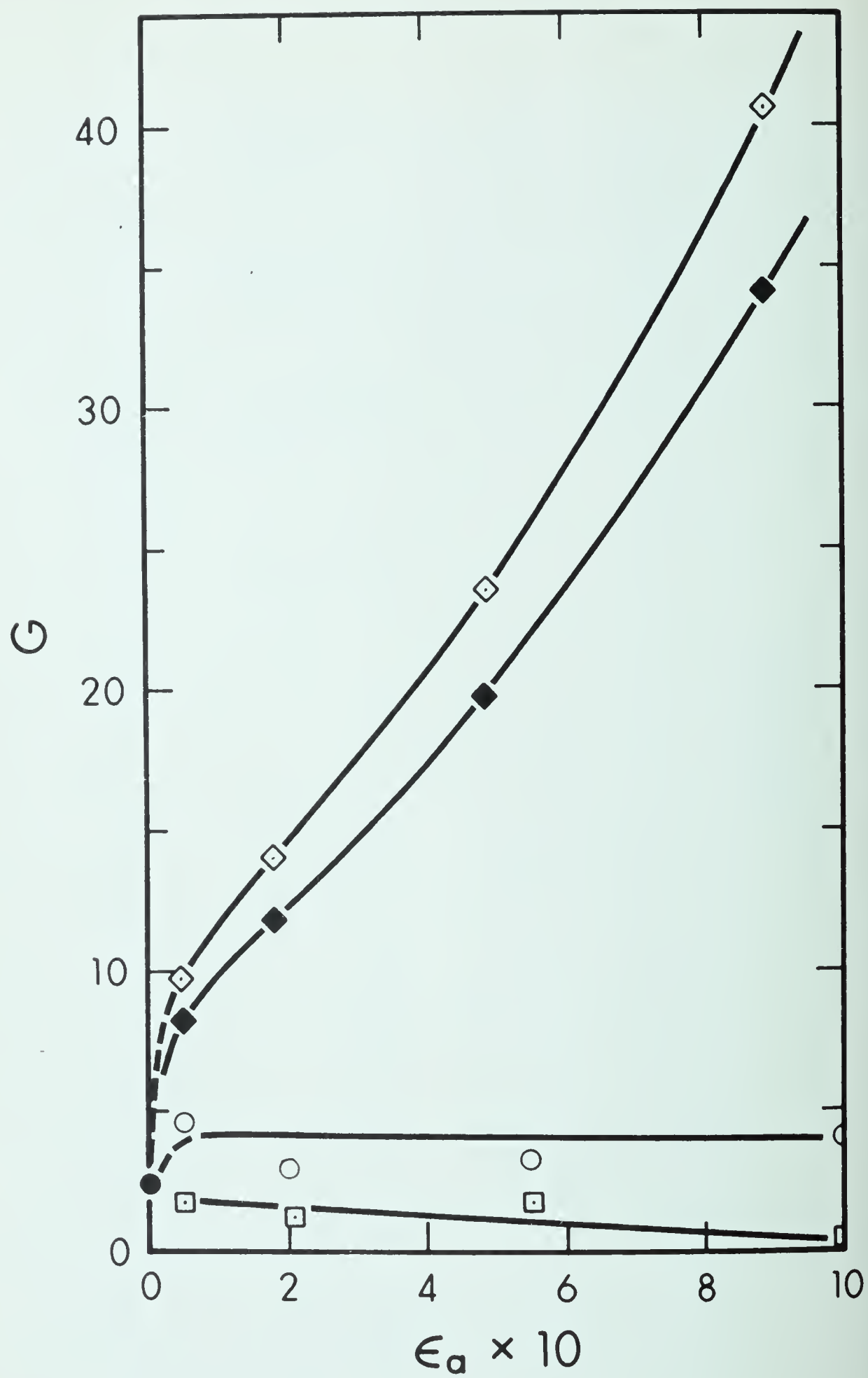


FIGURE III.14

Polymer Yields (Excluding Dimer) - Cyclohexene Solutions

- $\epsilon_a$  Electron fraction of additive
- Polymer yield from pure cyclohexene
- Added 1,4-cyclohexadiene
- Added benzene
- ◇ Added 1,3-cyclohexadiene
- ◆ Added 1,3-cyclohexadiene, with oxygen  
correction (see footnote on page 135 )



Two plots are given for the polymer yields from the solutions of 1,3-cyclohexadiene in cyclohexene, for the reason given in the footnote to Table III.22.

(6) 1,3-Cyclohexadiene

1,3-cyclohexadiene yields from the 1,4-cyclohexadiene/cyclohexene solutions are presented in Table III.15 and Figure III.11 A. The 1,3-diene and cyclohexene are poorly resolved by the 3,3'-oxydipropionitrile, so there is a considerable scatter in the results. A value of  $G = 0.55$  was obtained for the yield from pure 1,4-cyclohexadiene.

The disappearance of 1,3-cyclohexadiene from the solutions of 1,3-cyclohexadiene in cyclohexene was measured at low diene concentration, and the results are given in Table III.23 and Figure III.15. The rate of disappearance increased rapidly with increasing diene concentration to a value of  $G(-1,3\text{-cyclohexadiene}) = 14.7$  for a mixture with  $\epsilon_{1,3\text{-diene}} = 0.0202$ . Accurate measurements of the diene loss could not be made for higher concentrations of the 1,3-diene in cyclohexene, but the rapid increase in polymer formation, with increasing diene content (see Figure III.14), indicated that  $G(-1,3\text{-cyclohexadiene})$  must also be increasing rapidly.

(7) 1,4-Cyclohexadiene

No 1,4-cyclohexadiene production was detected in the radiolysis of the 1,3-cyclohexadiene/cyclohexene solutions, at the dose used.

1,4-cyclohexadiene disappearance from the 1,4-cyclohexadiene/cyclohexene



TABLE III.23

G-values for the Consumption of 1,3-Cyclohexadiene and 1,4-Cyclohexadiene from

Solutions of these Dienes in Cyclohexene

Electron fraction of 1,3-Diene	0.0017	0.00202	0.0103	0.0202
G( - 1,3-cyclohexadiene)	1.3	3.3	11.4	14.7

Electron fraction of 1,4-Diene	0.0054	0.0196
G( - 1,4-cyclohexadiene)	0.65	0.64



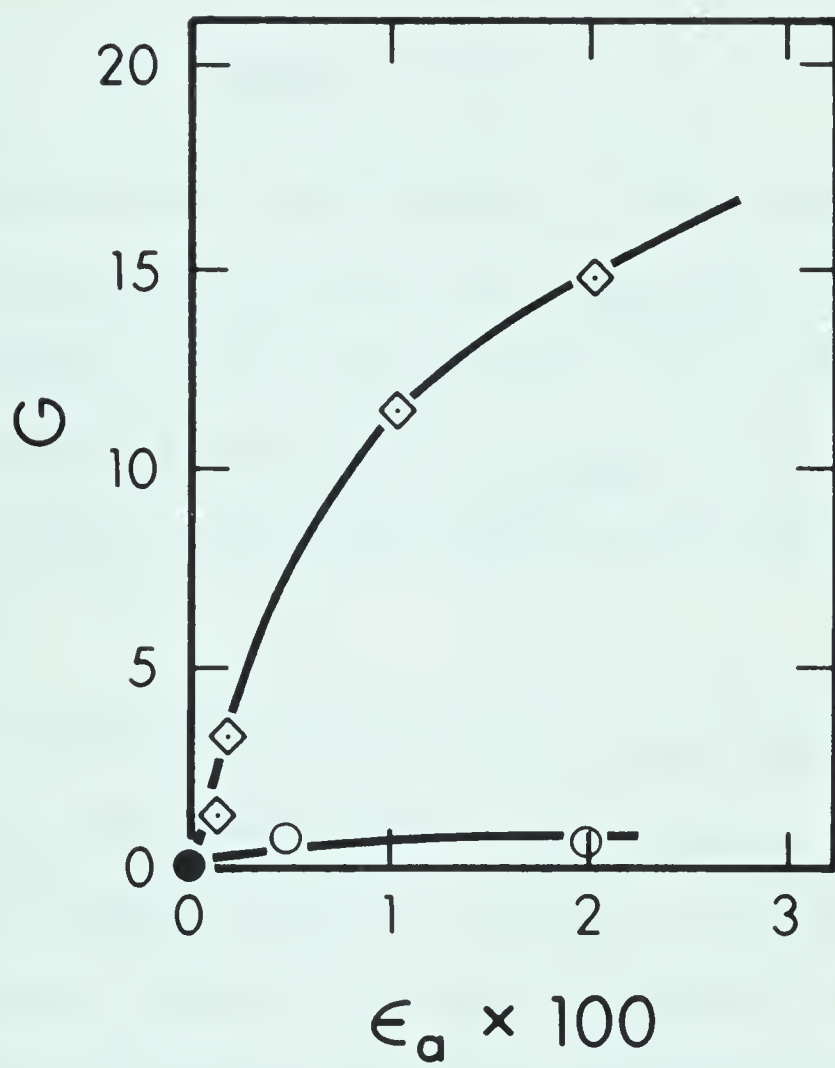
FIGURE III.15

Additive Disappearance from Cyclohexene Solutions

$\epsilon_a$       Electron fraction of additive

○      Added 1,4-cyclohexadiene

◇      Added 1,3-cyclohexadiene





solutions was measured at low diene concentrations and the results are given in Table III.23 and Figure III.15. It can be seen from the Figure that the 1,4-diene is considerably less reactive than the 1,3-diene in this system.

(8) Benzene

Benzene yields from the solutions of 1,3-cyclohexadiene in cyclohexene are presented in Table III.17, and Figure III.10A.  $G(\text{benzene})$  increased (from  $G < 0.05$  for pure cyclohexene) with the addition of 1,3-cyclohexadiene up to  $\epsilon_{1,3\text{-diene}} = 0.3$ . For higher concentrations of the 1,3-diene, the benzene yield appeared to be levelling off at  $G = 0.7$ .

Benzene formation occurred in the 1,4-cyclohexadiene/cyclohexene solutions as soon as they were opened to the air, so satisfactory determinations of  $G(\text{benzene})$  were not obtained. A value for  $G(\text{benzene}) = 0.9$  was obtained for the radiolysis of a specially purified sample of 1,4-cyclohexadiene, by analyzing for this product immediately after the sample was opened.

At a concentration of benzene in cyclohexene that was high enough to cause reasonable changes in the cyclohexene product yields,  $G(-\text{benzene})$  was not measurable. The much higher rate of disappearance of 1,3-cyclohexadiene from 1,3-diene/cyclohexene solutions had been barely measurable at a diene concentration equal to the lowest concentration of benzene used.



(9) Cyclohexene

Since no results were obtained from the radiolysis of pure 1,3-cyclohexadiene, no G-value for cyclohexene was obtained for the 1,3-diene.

No direct measurement of G(cyclohexene) was obtained for the radiolysis of pure 1,4-cyclohexadiene. A G-value for combined cyclohexene and 1,3-cyclohexadiene of 1.8 was obtained, using the di-n-decyl phthalate column. Subtraction of the 1,3-cyclohexadiene yield of  $G \approx 0.6$ , obtained using the 3,3'-oxydipropionitrile column, resulted in a value of  $G(\text{cyclohexene}) \approx 1.2$ .





(C) IRRADIATION OF "PURE" CYCLOHEXENE-d<sub>10</sub>

The deuterated cyclohexene used in this radiolysis contained 9.9%  $\text{c-C}_6\text{D}_9\text{H}$  as the main impurity. A dose of  $12.6 \times 10^{19}$  ev/g was absorbed. The measured product yields are given in column 1 of Table III.24. The corresponding values for the light cyclohexene radiolysis, at the same dose, are given in column 3 for comparison.

The yields of heavy hydrogen ( $G = 0.65$ ), cyclohexane ( $G = 0.66$ ) and 2,2'-dicyclohexenyl ( $G = 1.36$ ), from the deuterated cyclohexene, were less than those of their light counterparts from irradiated light cyclohexene. The yields of heavy dicyclohexyl ( $G = 0.47$ ), cyclohexylcyclohexene ( $G = 0.66$ ) and D-1 ( $G = 0.32$ ) were greater than those of the corresponding light compounds.



TABLE III.24

G-Values from Irradiation of Cyclohexene-d<sub>10</sub> and of a Solution of 1,3-Cyclohexadiene

in Cyclohexene-d <sub>10</sub>				
Product	1	2	3	4
	Cyclohexene-d <sub>10</sub>	1,3-Cyclohexadiene in Cyclohexene-d <sub>10</sub>	Cyclohexene	1,3-Cyclohexadiene in Cyclohexene
	Dose = 1.26 x 10 <sup>20</sup> ev/g	Dose = 1.42 x 10 <sup>20</sup> ev/g	Dose = ~1.2 x 10 <sup>20</sup> ev/g	Dose = ~1.2 x 10 <sup>20</sup> ev/g
Hydrogen	0.65	0.62*	1.28	1.23*
Cyclohexane	0.66	0.43	0.95	0.88
1,2'-Dicyclohexenyl	1.36	1.15	1.90	1.64
Cyclohexylcyclohexene	0.66	0.56	0.58	0.49
Cyclohexyl	0.47	0.38	0.21	0.18
1	0.32	0.30	0.22	0.18
Cyclohexadiene		1.55		0.74
Total Dimer (Silica-Gel)	2.81	3.94	2.91	3.23

The corresponding values for cyclohexene and 1,3-cyclohexadiene solution in cyclohexene are given for comparison. (Columns 3 and 4 respectively).

Dose rate = 7.6 x 10<sup>18</sup> ev/g hour. Electron fraction of 1,3-diene in solution = 0.0013 .

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Continued.....



TABLE III.24 (Continued)

Product	1	2	3	4
Total Dimer (Silicone Rubber)	2.57	3.74	3.46	4.12
Average Total Dimer	2.69	3.84	3.19	3.68
1,3-Cyclohexadiene		-4.3		-1.6
				- 144 -

\* Obtained by interpolation of results given in Figures, III.4 and III.16.





(D) IRRADIATION OF CYCLOHEXENE- $d_{10}$  WITH ADDED

---

1,3-CYCLOHEXADIENE

The electron fraction of added 1,3-cyclohexadiene was 0.0013 . The cyclohexene- $d_{10}$  used in this radiolysis contained 9.6%  $c-C_6D_9H$  . A dose of  $14.2 \times 10^{19}$  ev/g was absorbed. The product yields are given in column 2 of Table III.24. The corresponding values for a 1,3-cyclohexadiene/cyclohexene solution of the same constitution are given in column 4 for comparison.

The addition of this concentration of 1,3-cyclohexadiene to cyclohexene- $d_{10}$  reduced the yields of 2,2'-dicyclohexenyl, cyclohexylcyclohexene and dicyclohexyl by about the same degree that the yields of their hydrogenated counterparts were reduced by addition of the 1,3-diene to light cyclohexene. The cyclohexane yield seemed to be reduced more effectively in the cyclohexene- $d_{10}$  solution than it had been in the corresponding light cyclohexene solution, however. The yield of dicyclohexadiene was greater from the cyclohexene- $d_{10}$  solution. The rate of 1,3-cyclohexadiene disappearance was much higher from the cyclohexene- $d_{10}$  solution. The polymer yield from the cyclohexene- $d_{10}$  solution was not measured.



(E)  $H_2$ , HD AND  $D_2$  YIELDS FROM CYCLOHEXENE- $d_{10}$ ,  
WITH ADDITIVES

---

Binary solutions of cyclohexene- $d_{10}$  with added 1,4-cyclohexadiene, benzene and 1,3-cyclohexadiene were irradiated. Also a 50/50 solution of heavy and light cyclohexene was irradiated with, and without, added 1,3-cyclohexadiene. Variations in the yields of  $H_2$ , HD and  $D_2$  were studied as a function of the electron fraction of the additives,  $\epsilon_a$ . The product fraction not condensable at  $-196^\circ\text{C}$  was considered to be  $H_2$ , HD and  $D_2$  only. A portion of the gas collected in the McCleod-Toepler gauge was analyzed by the mass-spectrometer in order to determine the  $H_2 : HD : D_2$  ratio. The results are given in Table III.25. The total yields i.e.  $G(H_2 + HD + D_2)$  values are compared, in Figure III.16, with the hydrogen yields from the corresponding mixtures with light cyclohexene. The hydrogen yields from the cyclohexene solutions are represented by the dash-dot lines. These lines are reproductions of the curves given in Figure 4. For all the solutions radiolyzed the yield of hydrogen was reduced by the substitution of cyclohexene- $d_{10}$  for cyclohexene. The degree of inhibition due to a given additive was, however, similar for both light and heavy cyclohexene solutions. The lines representing  $G(\text{hydrogen})_{\text{ex}}$  were left out of Figure III.16 for clarity.





TABLE III.25

H<sub>2</sub>, D<sub>2</sub> and HD Yields from Solutions of Cyclohexene, 1,3-Cyclohexadiene, 1,4-Cyclohexadiene and Benzene

in Cyclohexene-d<sub>10</sub>

Dose rate = 7.65 x 10<sup>18</sup> ev/g hour.

Dose range = 1.02 - 1.54 x 10<sup>20</sup> ev/g.

ELECTRON FRACTIONS OF COMPONENTS IN SOLUTIONS					G-VALUES				
$c-C_6D_{10}$	$c-C_6D_9H^*$	$c-C_6H_{10}$	$1,3-c-C_6H_8$	$1,4-c-C_6H_8$	$C_6H_6$	$H_2$	HD	$D_2$	TOTAL
0.880	0.120					0.008	0.039	0.604	0.65
0.813	0.086	0.003	0.098			0.030	0.092	0.238	0.36
0.359	0.038	0.018	0.585			0.142	0.073	0.025	0.24
0.790	0.108			0.102		0.087	0.229	0.374	0.69
0.347	0.047			0.606		0.690	0.242	0.039	0.97
0.789	0.108				0.103	0.007	0.063	0.440	0.51
0.343	0.047				0.610	0.025	0.052	0.083	0.16
0.440	0.060	0.500				0.463	0.378	0.129	0.97
0.396	0.054	0.453	0.098			0.292	0.206	0.062	0.56
0.174	0.024	0.216	0.585			0.227	0.055	0.008	0.29

\* Cyclohexene  $d_{10}$  contained 12.0%  $c-C_6D_9H$  (Batch 1) and

\* Cyclohexene d<sub>10</sub> contained 12.0% c-C<sub>6</sub>D<sub>9</sub>H (Batch 1) and 9.6% c-C<sub>6</sub>D<sub>9</sub>H (Batch 2)



FIGURE III.16

Hydrogen Yields - Cyclohexene-d<sub>10</sub> Solutions

- $\epsilon_a$  Electron fraction of additive
- Hydrogen yield from pure cyclohexene
- Corresponding hydrogen yields from light  
cyclohexene solutions

A

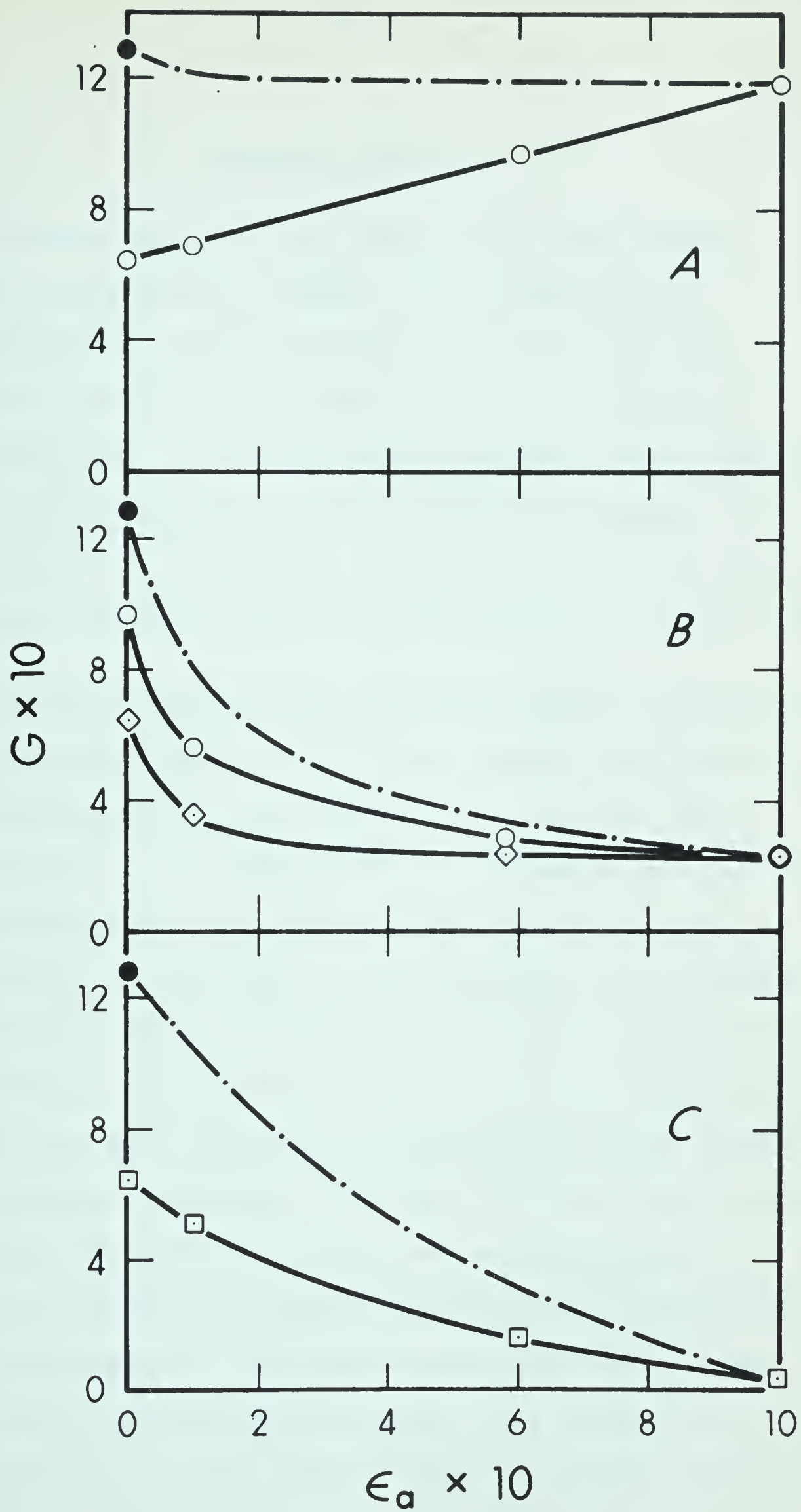
Added 1,4-cyclohexadiene

B

- ◇ 1,3-cyclohexadiene added to cyclohexene-d<sub>10</sub>
- 1,3-cyclohexadiene added to a 50/50 solution  
of cyclohexene and cyclohexene-d<sub>10</sub>

C

Added benzene





(F) APPEARANCE POTENTIALS

Appearance potentials were determined for singly ionized cyclohexene, cyclohexene-d<sub>10</sub>, benzene, 1,4-cyclohexadiene and 1,3-cyclohexadiene. The full experimental results obtained for these ions are given in Tables III.26, III.27, III.28, III.29 and III.30, respectively. In each case the corresponding results obtained for singly ionized xenon, the internal standard, are included. The results are plotted in Figures III.17, III.18, III.19, III.20 and III.21, respectively, in accordance with the method described by Lossing et al (90).

The values obtained for the appearance potentials of these five ions are summarized in Table III.31. (Cyclohexene)<sup>+</sup>, (cyclohexene-d<sub>10</sub>)<sup>+</sup> and (1,4-cyclohexadiene)<sup>+</sup> had the same value of 9.2 volts, within experimental error. The results obtained in the determination of these three potentials gave two parallel straight lines near the threshold voltage in each of Figures III.17, III.18 and III.20. It is necessary that such parallel straight lines shall be obtained, if reliable results are to be obtained by this method. It can be seen from Figures III.19 and III.21, that the results obtained in the determination of the (benzene)<sup>+</sup> and (1,3-cyclohexadiene)<sup>+</sup> appearance potentials, did not give rise to parallel straight lines. Thus the results for these two compounds must be considered less reliable than those for (cyclohexene)<sup>+</sup>, (cyclohexene-d<sub>10</sub>)<sup>+</sup> and (1,4-cyclohexadiene)<sup>+</sup>. There seems little doubt however, that, under the experimental conditions used, (benzene)<sup>+</sup> had a higher, (9.9 V), and (1,3-cyclohexadiene)<sup>+</sup> a lower, (8.7 V) appearance potential than (cyclohexene)<sup>+</sup>.



TABLE III.26

Appearance Potential Data for Cyclohexene

APPLIED VOLTAGE	$\text{c-C}_6\text{H}_{10}^+$			APPLIED VOLTAGE	$\text{Xe}^+$	
	PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V				PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V	
	1	2	3		1	2
10.0	6.42	6.64	6.55	12.6	4.97	5.01
9.8	5.12	5.32	5.28	12.4	4.08	4.08
9.6	4.24	4.26	4.28	12.2	3.18	3.19
9.4	3.30	3.36	3.27	12.0	2.36	2.31
9.2	2.45	2.62	2.56	11.8	1.63	1.67
8.0	1.81	1.97	1.94	11.6	1.00	1.01
8.8	1.21	1.36	1.35	11.4	0.553	0.562
8.6	0.735	0.837	0.820	11.2	0.283	0.302
8.4	0.362	0.467	0.407	11.0	0.131	0.125
8.2	0.182	0.227	0.187			
8.0		0.103				

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TABLE III.27

Appearance Potential Data for Cyclohexene-d<sub>10</sub>

APPLIED VOLTAGE	c-C <sub>6</sub> D <sub>10</sub> <sup>+</sup>			APPLIED VOLTAGE	Xe <sup>+</sup>	
	PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V				PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V	
	1	2	3		1	2
10.0	6.90	6.80	6.55	12.8	5.62	5.68
9.8	5.50	5.42	5.27	12.6	4.83	4.82
9.6	4.40	4.37	4.19	12.4	4.01	4.00
9.4	3.43	3.36	3.26	12.2	3.16	3.18
9.2	2.70	2.61	2.53	12.0	2.32	2.32
9.0	2.02	1.95	1.94	11.8	1.68	1.66
8.8	1.38	1.35	1.36	11.6	1.04	1.03
8.6	0.866	0.830	0.805	11.4	0.565	0.552
8.4	0.478	0.464	0.465	11.2	0.320	0.300
8.2	0.225	0.232	0.229	11.0	0.141	0.140
8.0	0.096	0.099	0.099			

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TABLE III.28

Appearance Potential Data for Benzene

APPLIED VOLTAGE	$C_6H_6^+$			APPLIED VOLTAGE	$Xe^+$	
	1	2	3		1	2
11.0	5.48		5.68	12.8	5.63	5.78
10.8	4.83	4.83	5.00	12.6	4.71	4.79
10.6	4.22	4.12	4.36	12.4	3.78	3.83
10.4	3.61	3.47	3.69	12.2	2.92	2.91
10.2	2.87	2.83	3.02	12.0	2.04	2.12
10.0	2.21	2.18	2.43	11.8	1.38	1.47
9.8	1.70	1.67	1.82	11.6	0.840	0.900
9.6	1.29	1.23	1.36	11.4	0.525	0.550
9.4	0.880	0.847	0.952	11.2	0.313	0.338
9.2	0.605	0.525	0.643	11.0	0.196	0.210
9.0	0.357	0.324	0.397	10.8	0.118	0.131
8.8	0.197	0.176	0.224			
8.6	0.100		0.121			



TABLE III.29

Appearance Potential Data for 1,4-Cyclohexadiene

APPLIED VOLTAGE	1,4-c-C <sub>6</sub> H <sub>8</sub> <sup>+</sup>			APPLIED VOLTAGE	Xe <sup>+</sup>	
	PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V				PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V	
	<u>1</u>	<u>2</u>	<u>3</u>		<u>1</u>	<u>2</u>
10.2	6.22	6.05		12.6	4.87	4.88
10.0	5.01	4.87	4.68	12.4	4.01	4.03
9.8	4.03	3.90	3.77	12.2	3.18	3.15
9.6	3.20	3.08	3.00	12.0	2.31	2.30
9.4	2.48	2.41	2.32	11.8	1.66	1.68
9.2	1.96	1.96	1.67	11.6	1.02	0.990
9.0	1.47	1.50	1.41	11.4	0.570	0.557
8.8	1.04	1.09	1.00	11.2	0.283	0.276
8.6	0.720	0.735	0.655	11.0	0.138	0.124
8.4	0.413	0.462	0.383			
8.2	0.217	0.249	0.208			
8.0	0.112	0.123				





TABLE III.30

Appearance Potential Data for 1,3-Cyclohexadiene

<u>1,3-c-C<sub>6</sub>H<sub>8</sub><sup>+</sup></u>		<u>Xe<sup>+</sup></u>	
APPLIED VOLTAGE	PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V		
	<u>1</u>	<u>2</u>	<u>3</u>
9.0	5.43	5.50	5.43
8.8	4.52	4.81	4.62
8.6	3.52	3.80	3.61
8.4	2.52	2.59	2.60
8.2	1.61	1.76	1.67
8.0	0.927	1.03	0.990
7.8	0.538	0.618	0.542
7.6	0.273	0.350	0.285
7.4	0.110	0.144	0.125

APPLIED VOLTAGE	PEAK HEIGHT x 100/PEAK HEIGHT AT 60 V	
	<u>1</u>	<u>2</u>
12.6	4.99	5.02
12.4	4.17	4.17
12.2	3.27	3.27
12.0	2.40	2.44
11.8	1.76	1.74
11.6	1.07	1.12
11.4	0.627	0.645
11.2	0.373	0.376
11.0	0.211	0.236
10.8	0.138	0.132

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FIGURE III.17

Appearance Potential Data for Cyclohexene

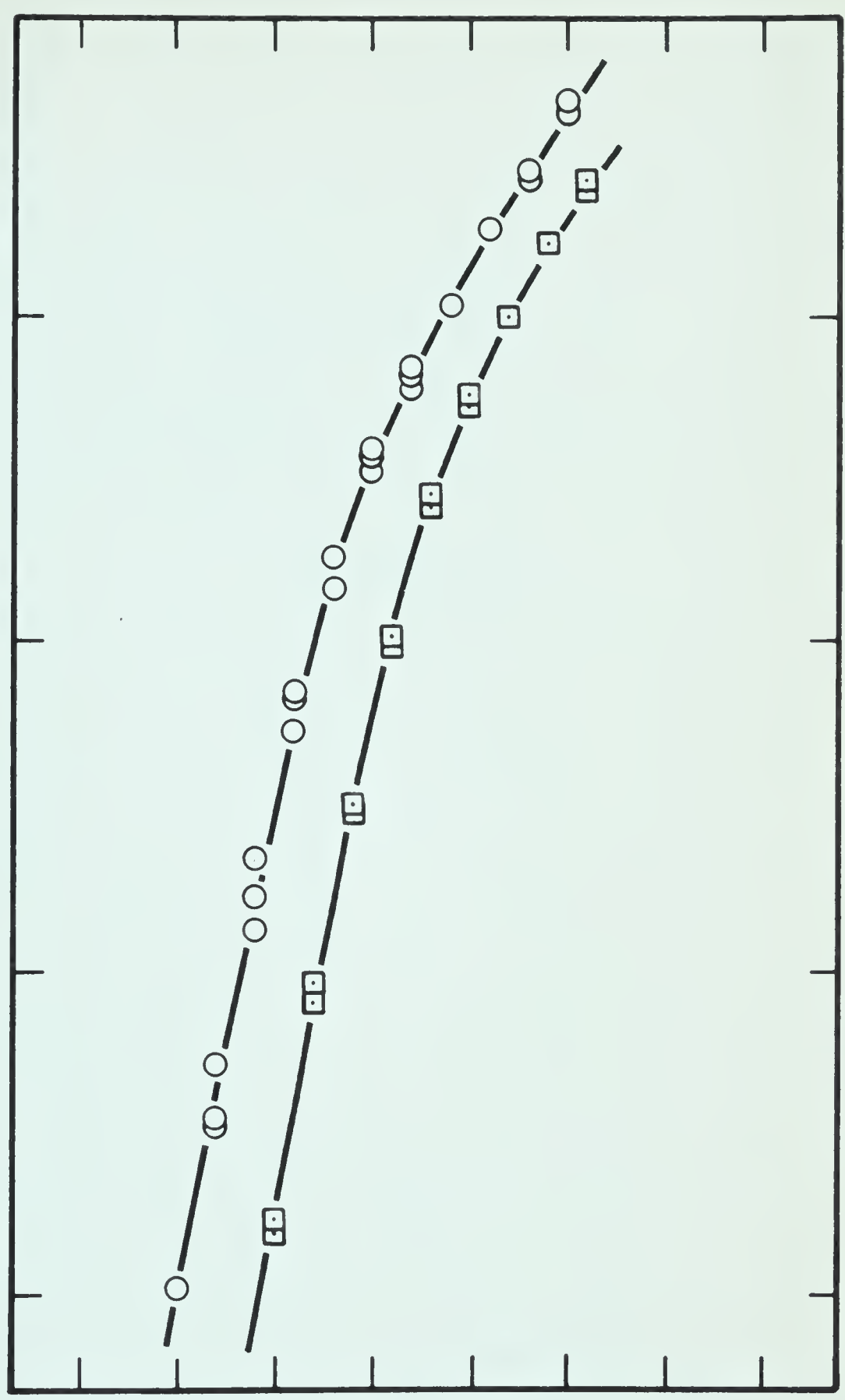
○ Cyclohexene

□ Xenon

LOG [% OF PEAK AT 60 V]

0.5  
0.0  
-0.5  
-1.0

c - C<sub>6</sub> H<sub>10</sub> SCALE  
XENON SCALE

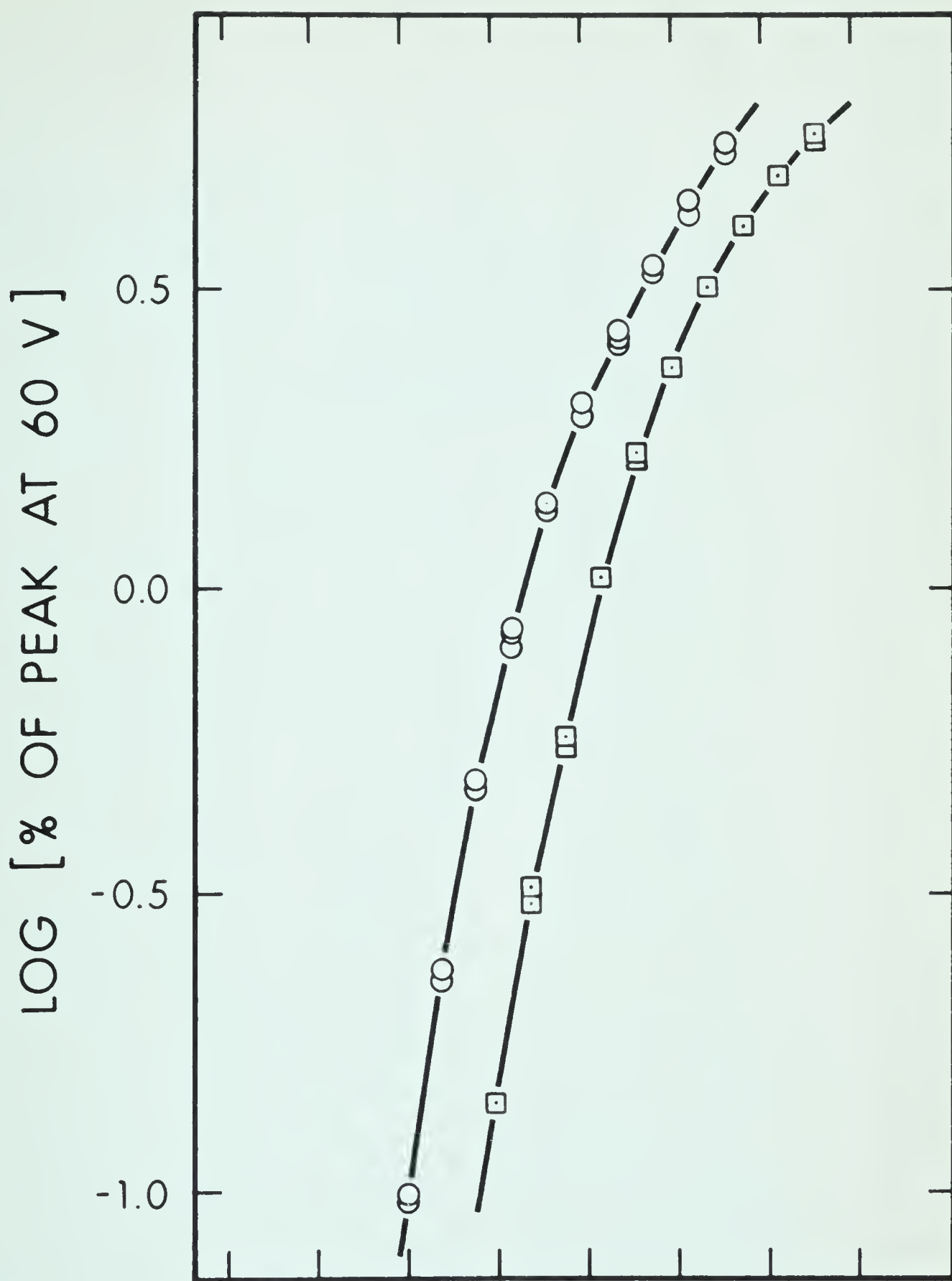


VOLTS

FIGURE III.18

Appearance Potential Data for Cyclohexene-d<sub>10</sub>

- Cyclohexene-d<sub>10</sub>
- Xenon



c - C<sub>6</sub> D<sub>10</sub> SCALE  
XENON SCALE

VOLTS



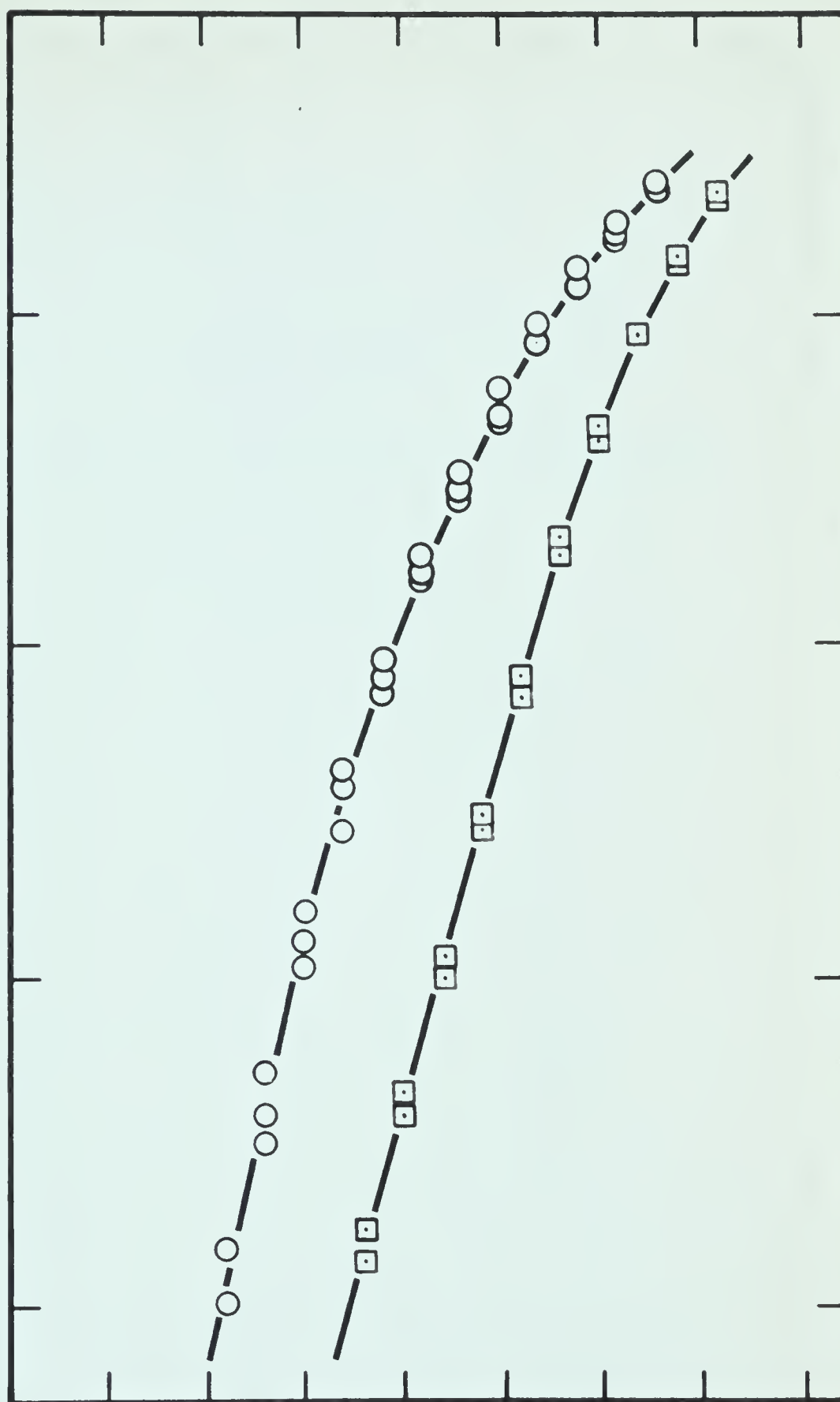
FIGURE III.19

Appearance Potential Data for Benzene

- Benzene
- Xenon

LOG [% OF PEAK AT 60 V]

0.5  
0.0  
-0.5  
-1.0



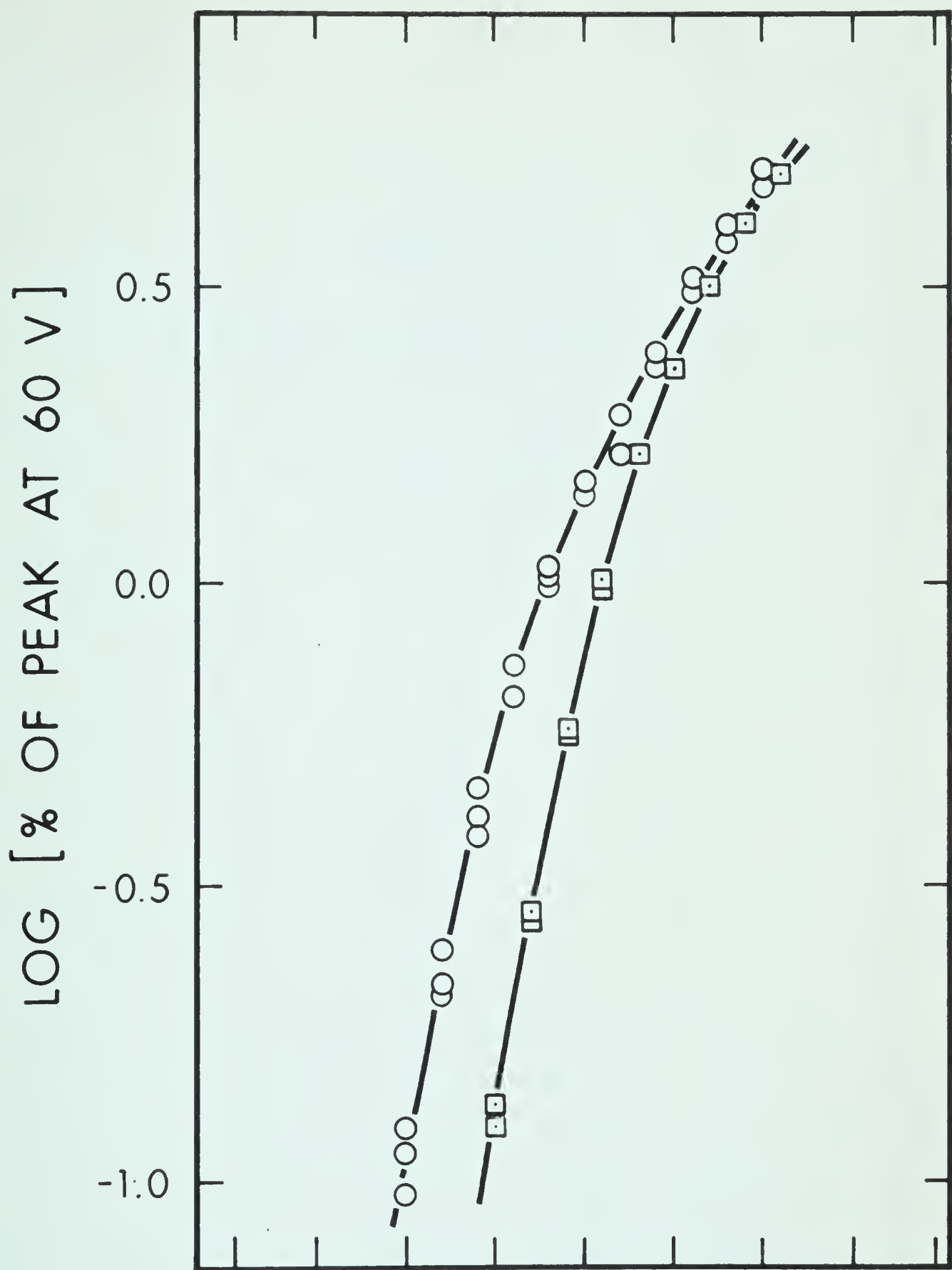
$C_6H_6$  SCALE  
XENON SCALE

VOLTS

FIGURE III.20

Appearance Potential Data for 1,4-Cyclohexadiene

- 1,4-cyclohexadiene
- Xenon



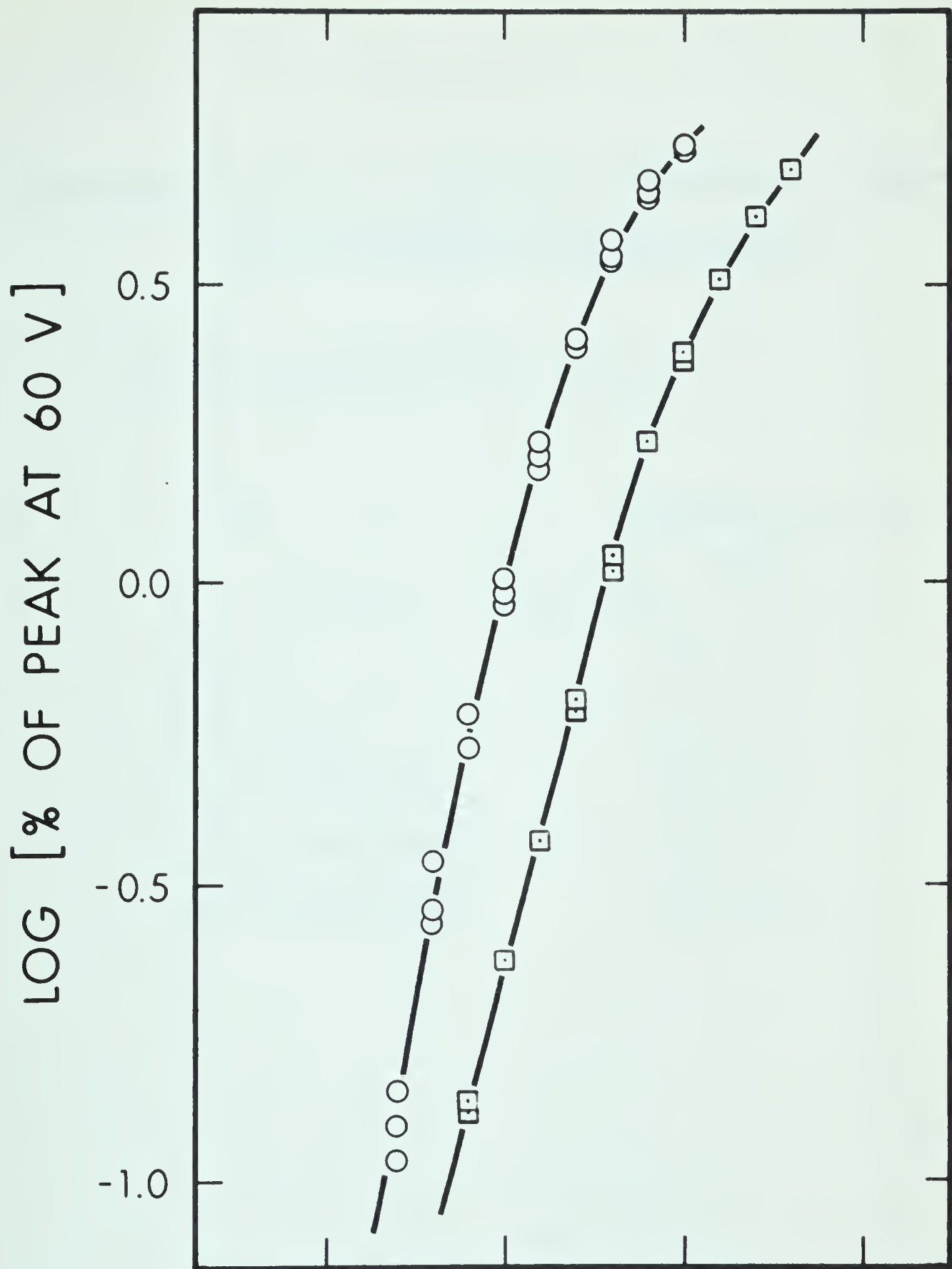
$c\text{-C}_6\text{H}_8$  SCALE  
XENON SCALE

VOLTS

FIGURE III.21

Appearance Potential Data for 1,3-Cyclohexadiene

- 1,3-cyclohexadiene
- Xenon



$c\text{-C}_6\text{H}_8$  SCALE  
XENON SCALE

VOLTS





TABLE III.31

Appearance Potentials for Cyclohexene, Cyclohexene-d<sub>10</sub>, Benzene,  
1,4-Cyclohexadiene and 1,3-Cyclohexadiene

Appearance potential for  $\text{Xe}^+ = 12.127$

ION	APPEARANCE POTENTIAL
	VOLTS
(benzene) <sup>+</sup>	9.9 ± 0.3
(cyclohexene) <sup>+</sup>	9.2 ± 0.2
(cyclohexene-d <sub>10</sub> ) <sup>+</sup>	9.2 ± 0.2
(1,4-cyclohexadiene) <sup>+</sup>	9.2 ± 0.2
(1,3-cyclohexadiene) <sup>+</sup>	8.7 ± 0.3



#### SECTION IV - DISCUSSION



#### SECTION IV    -    DISCUSSION

In part (A) of this discussion mechanistic conclusions that can be drawn with confidence from the experimental data will be reviewed. In part (B) mechanisms that are consistent with the experimental data will be presented and their feasibility discussed. In part (C) the effects of additives on the cyclohexene radiolytic system will be discussed. Overall conclusions will be presented in section (D).





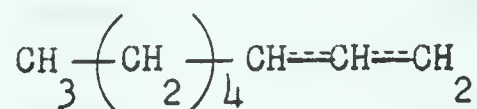
(A) MECHANISTIC CONCLUSIONS DRAWN FROM THE EXPERIMENTAL DATA

(1) 2,2'-Dicyclohexenyl is Formed Almost Exclusively by Radical-Radical Combination

2,2'-Dicyclohexenyl is the principal dimeric product of the free radical induced reaction of cyclohexene (81). The reaction intermediate is the resonance stabilized 2-cyclohexenyl radical, shown below.



Resonance stabilized radicals of this type are characteristic intermediates in the free radical dimerization of any olefins that have a hydrogen atom in the  $\beta$  position. For example, in the free radical dimerization of 1-octene (66) the intermediate is



Evidence for the presence of the 2-cyclohexenyl radical in the liquid cyclohexene radiolytic system is as follows. This radical species has been detected by E.S.R. spectrometry in cyclohexene under the influence of radiation (32). The predominant dimeric product in the radiolysis of liquid cyclohexene was 2,2'-dicyclohexenyl (~65% of the total dimer yield), and it was the only di-olefinic dimer formed. The only mono-olefinic dimer formed was 3-cyclohexylcyclohexene, which can be formed by combination of a



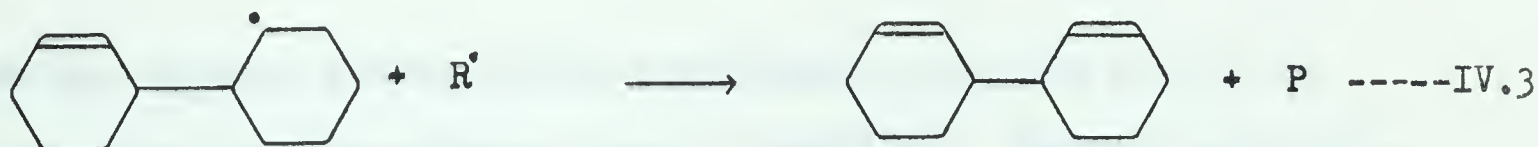
2-cyclohexenyl radical and a cyclohexyl radical.\*

Thus a most probable mechanism for the formation of 2,2'-dicyclohexenyl is that given in step IV.1.



Other processes for the formation of this dimeric product were considered and found to be unsatisfactory. Some of these will be discussed below.

Processes involving cyclohexenyl radical addition to cyclohexene were tried (Step IV.2). The second step in the process must be radical-radical disproportionation, as shown in IV.3, if a di-olefin is to result.



where P is a stable product

---

\* Ohnishi and Nitta (32) detected two radicals in irradiated cyclohexene.

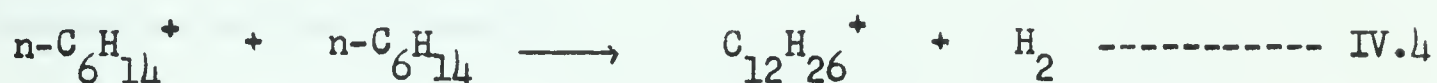
One was apparently the 2-cyclohexenyl radical. The other was not identified but presumably could have been the cyclohexyl radical.



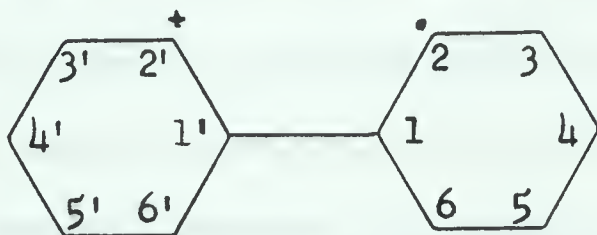


Many identities for R' were tried, but no self-consistent mechanism could be formulated that included these reactions, and at the same time explain the experimental results.

No reasonable ionic mechanism could be formulated to explain production of 2,2'-dicyclohexenyl that did not include the formation of 2-cyclohexenyl radicals, which then reacted to give the dimer. Kevan and Libby have suggested a direct ionic dimerization mechanism for n-hexane, radiolyzed in the solid phase (93) (94). This was



The intermediate for such a reaction in cyclohexene would be



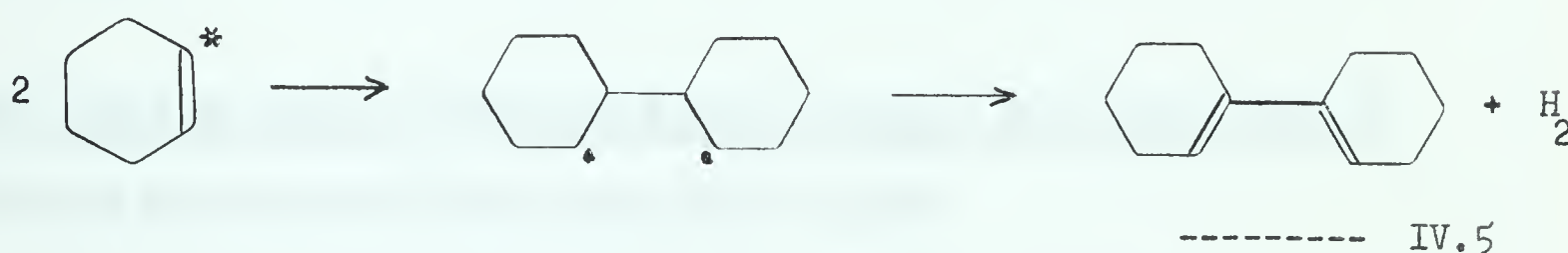
To form the required dimeric product, hydrogen atoms would have to be eliminated from the non-adjacent 3 and 3' positions. There is negligible overlap between the hydrogen orbital in a 3-position on the molecule and any orbital in the other ring, so such a process appears most improbable. A far more likely process for this species would be hydride ion transfer from position 1 to position 2', yielding 1-cyclohexylcyclohexene on neutralization. If elimination of molecular hydrogen were to take place as a result of the energy of neutralization, the most probable dimeric product





would appear to be the conjugated 1,1'-dicyclohexenyl.

If direct dimerization of two excited molecules was to occur, the most likely product would again be the 1,1'-dicyclohexenyl as shown by



where \* denotes an excited molecule.

(2)  $k_d/k_c$  for Cyclohexenyl Radicals is  $< 0.1$

---

The combined yield of 1,3- and 1,4-cyclohexadiene was  $< 0.15$ .

Thus if it were correct to conclude that 2,2'-dicyclohexenyl was formed by cyclohexenyl radical combination only, the disproportionation/combination ratio for cyclohexenyl radicals,  $k_{IV.7}/k_{IV.6}$ , must be  $< 0.1$ .\*

---

\* The observed yields of 1,3- and 1,4-cyclohexadiene were approximately equal to the true initial yields of these compounds, since cyclohexadiene consumption is a very minor process at low concentration of these dienes present in irradiated pure cyclohexene. The observed values for  $G(1,3\text{-cyclohexadiene})$  and  $G(1,4\text{-cyclohexadiene})$  were  $< 0.1$  and  $\sim 0.05$  respectively. Values for cyclohexadiene consumption, obtained by extrapolation (see Figure III) are  $\sim 0.02$  and  $< 0.02$  for  $G(1,3\text{-cyclohexadiene})$  and

(Continued on next page)



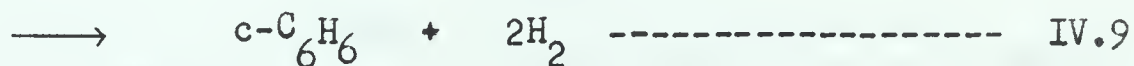
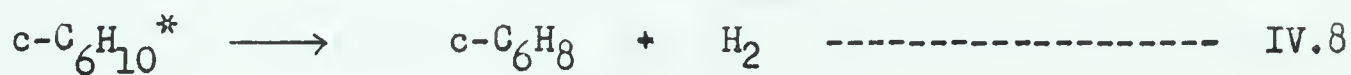


(3) The Yield of Molecular Hydrogen Formed by Direct Elimination from an Excited Cyclohexene Molecule must be  $G < 0.25$

The yield of the cyclohexadiene was  $G < 0.15$  and of benzene  $< 0.05$  .

Thus the yield of hydrogen formed in processes IV.8 and IV.9 must be

$$G < 0.25$$



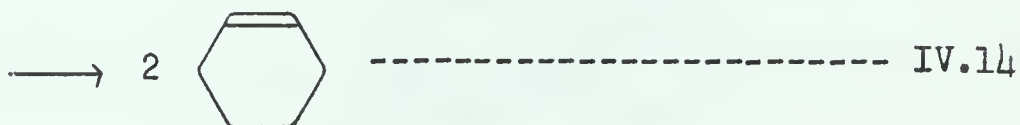
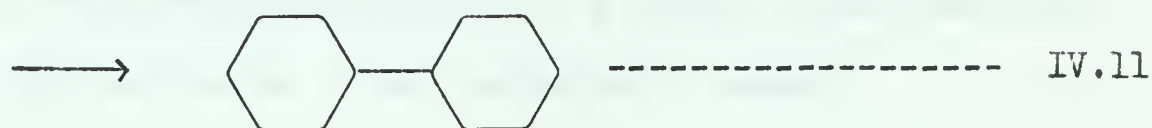
where \* denotes an excited molecule.

G(-1,4-cyclohexadiene) respectively, for the highest concentration of these dienes that could possibly be present in irradiated pure cyclohexene.



(4) Cyclohexane Cannot Arise from Radical Disproportionation Alone

The radical reactions concerned are



The observed yield of cyclohexane is  $G = 0.95$ , of dicyclohexyl is  $G = 0.23$  and of 3-cyclohexylcyclohexene is  $G = 0.6$ .

Since the combined yields of 1,3- and 1,4-cyclohexadiene are  $< 0.15$ , the yield of cyclohexane from step IV.12 cannot be more than this value. Thus the ratio  $k_{\text{IV.10}}/k_{\text{IV.11}}$  would have a value 3.5 - 4.1 if all the cyclohexane and dicyclohexyl observed were produced in the above steps. If some dicyclohexyl were formed in a different way then value of this ratio would be still higher. Values for  $k_{\text{IV.10}}/k_{\text{IV.11}}$  have been reported as 1.31 - 1.47 (95) (11), so

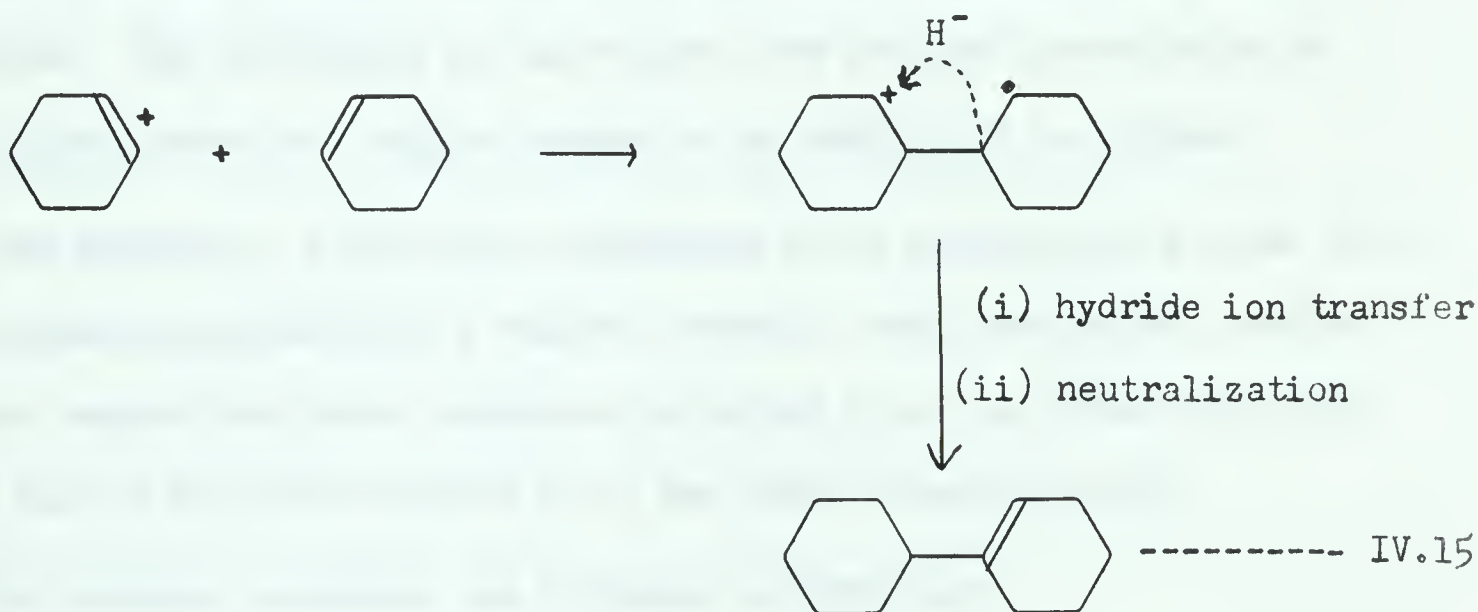




that not all of the cyclohexane produced in the radiolysis could be formed by reactions IV.10 and IV.12.

(5) An Ionic Dimerization Process of the Type Suggested for 1-Hexene is Absent

The absence of 1-cyclohexylcyclohexene as a product indicates that the following process does not occur to any appreciable extent



This is the ionic dimerization process suggested for the 1-hexene (28) and 1-butene (68) radiolyses (see section I (B) (c) (1) ). A study of this process using Stuart-Briegleb orbital models indicated that there was negligible overlap at the ionic site for an H-atom in the 3-position, so the observed 3-cyclohexylcyclohexene is not an expected product of this reaction.

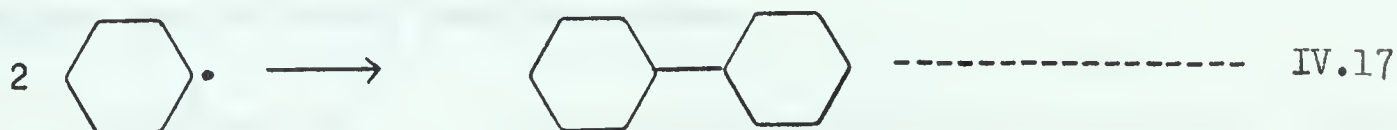


(6) Any Given Radical Species Must React Either Almost Exclusively by a First Order or Almost Exclusively by a Second Order Mechanism, Over the Dose Rate Range Studied

In this work the yields of products from cyclohexene were studied over the dose rate range  $1.3 \times 10^{17}$  -  $2.6 \times 10^{19}$  ev/g hour. Burns and Winter have reported product yields for dose rates of  $1.2 \times 10^{19}$  ev/g hour ( $\gamma$ -rays) and  $\sim 6 \times 10^{22}$  ev/g hour (4 Mev electrons) (80). The G-values for dicyclohexane, 3-cyclohexylcyclohexene and dicyclohexyl are given as a function of dose rate in Figure IV.1. No marked dose rate effect is observable for the products over the dose rate range covered by the two laboratories. The difference in the values from the two laboratories in the overlapping dose rate region appears to be analytical in origin.

The absence of a dose rate dependence for a product yield means that if that product resulted from a radical reaction, then the radical reactant could have reacted only with substrate molecules (i.e. 1st order reactions only) or only with other radicals (i.e. 2nd order reactions only).

For example, consider the following competition



If reaction IV.16 and one or both of reactions IV.17 and IV.18 occur at a similar rate in a given dose rate region, then there will be a dose rate dependence in the yields of cyclohexane and dicyclohexyl in that dose rate





region. This is shown by the relationships IV.19 and IV.20

$$\frac{G(\text{cyclohexane})}{G(\text{dicyclohexyl})} = \frac{k_{\text{IV.16}} [\text{Cyclohexane}] [\text{Cyclohexyl}^\bullet] + k_{\text{IV.18}} [\text{Cyclohexyl}^\bullet]^2}{k_{\text{IV.17}} [\text{Cyclohexyl}^\bullet]^2} \quad \text{IV.19}$$

$$= \frac{A}{[\text{Cyclohexyl}^\bullet]} + B \quad \text{IV.20}$$

where A and B are constants.

Thus the relative rates of cyclohexane and dicyclohexyl formation are dependent on the concentration of cyclohexyl radicals, which in turn is dependent on the dose rate.

It is of interest to determine approximately in what dose rate region this dose rate dependence might be expected to occur, and to determine its probable character.

#### (i) Nature of the Dose Rate Dependence

Consider the following reaction scheme

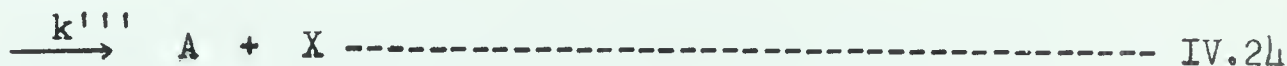




FIGURE IV.1

G-Values as a Function of Dose Rate -

Cyclohexene System

Burns and  
Winter (80)

This work



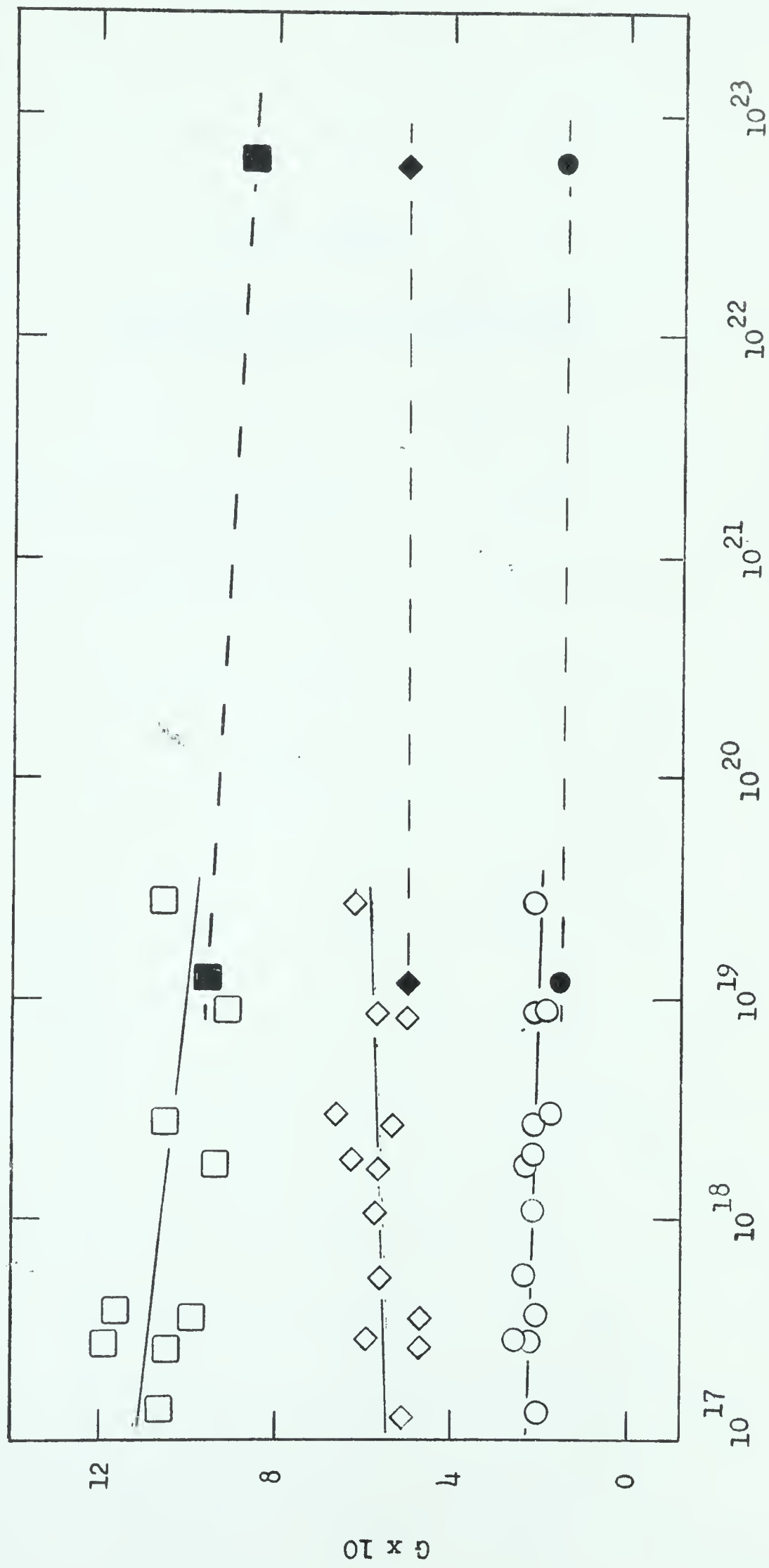
Cyclohexane



3-Cyclohexylcyclohexene



Dicyclohexyl



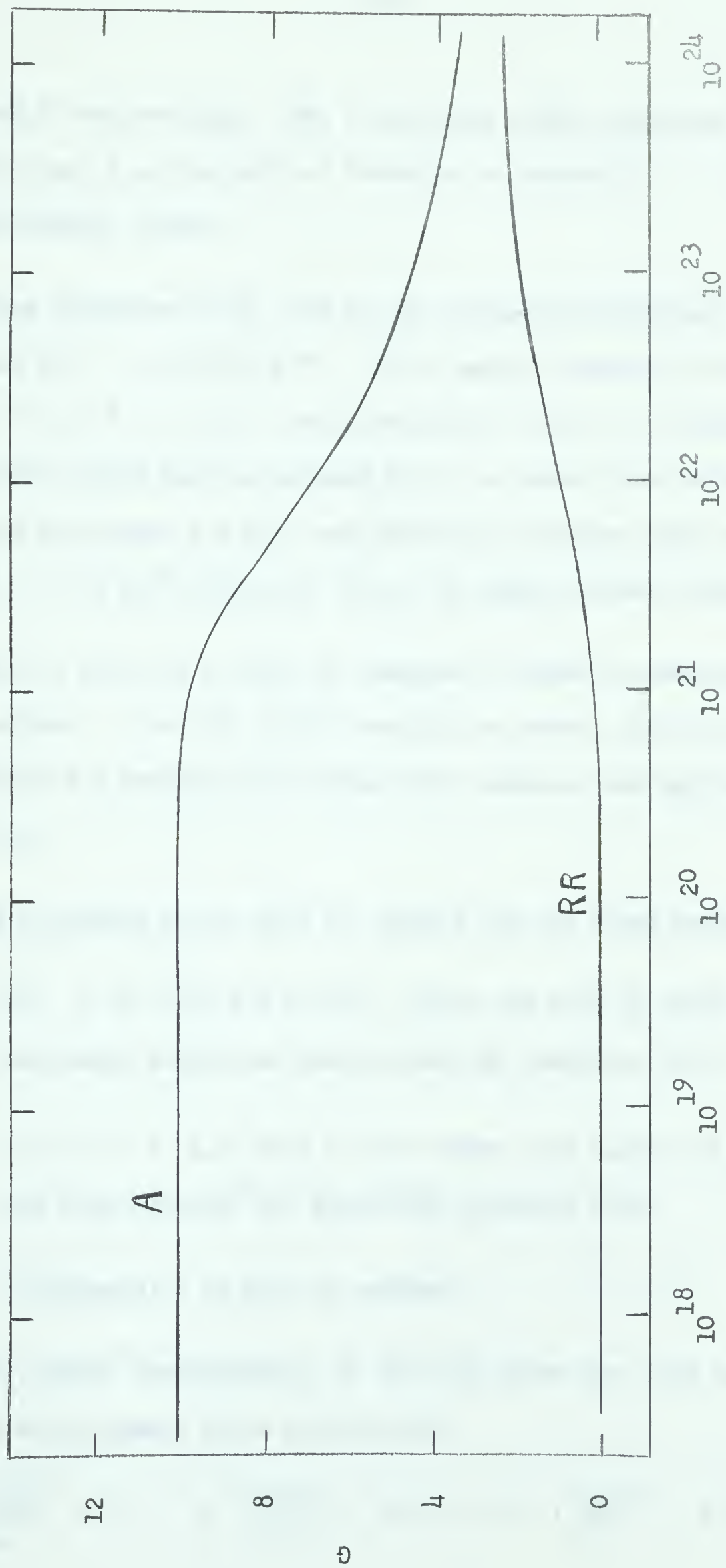
Dose Rate (ev/g hour)

FIGURE IV.2

Hypothetical Dose Rate Dependence

A, RR

Stable Products - see calculation  
on page 170.



Dose Rate (ev/g hour)



Where  $R'$  and  $R^\bullet$  are radicals.  $RR$ ,  $X$  and  $A$  are stable products,  $M$  is the substrate and  $I$  is the rate of formation of radical  $R^\bullet$ . (IV.21 may include several steps).

Since reactions IV.23 - IV.25 are diffusion controlled, it follows that  $(k'' + k''') \approx k^v$ . If we assign reasonable values for  $(k'' + k''')$ ,  $k^v$ ,  $k'''/k''$  and  $G(\text{radicals})$ , then it is possible to determine what values must be assumed for  $k'$  in order that there shall be no dose rate dependence for  $G(A)$  and  $G(RR)$  over the dose rate range  $1.3 \times 10^{17} - 6 \times 10^{22}$  ev/g hour, (i.e. the range covered experimentally).

First a value of  $k'$  will be assigned in order to demonstrate the dose rate effect.  $k' = 230$  l/mole sec will be taken, since this is the value reported for reaction IV.22 when ethyl radicals and cyclohexene are involved (71).

The following values will be assumed for the other parameters

$(k'' + k''') \approx k^v \approx 10^{10}$  l/mole sec will be taken for the diffusion controlled radical-radical reactions (73).

$k'''/k'' = 1.31$  will be used since this value for the ratio has been reported for cyclohexyl radicals (95).

$G(\text{radicals}) = 10$  will be assumed.

The radical concentration  $R^\bullet$  for any given dose rate may be obtained from the steady state relationship

$$\frac{d[R^\bullet]}{dt} = I - k' [M][R^\bullet] - 2(k'' + k''') [R^\bullet]^2 - k^v [R^\bullet][R'] = 0$$





In the dose rate region where  $R^\bullet$  reacts predominantly by step IV.22,  $[R^\bullet]$  is given by

$$[R^\bullet] \approx \frac{I}{k' [M]} \approx \frac{I}{10k'} \quad \text{----- IV.27}$$

Since  $[M] \approx 10$  mole/l in this system.

In the dose rate region where  $R^\bullet$  reacts predominantly by steps IV.23 - IV.24, the concentration of  $R^\bullet$  is given by

$$[R^\bullet] = \sqrt{\frac{I}{2(k'' + k''')}} \approx \sqrt{\frac{I}{10^{10}}} \quad \text{----- IV.27}$$

Using the value  $k' = 230$  l/mole sec, and plotting resulting values of  $G(A)$  and  $G(RR)$  against dose rate, gives the plots shown in Figure IV.2. It can be seen that, for this value of  $k'$ ,  $G(A)$  and  $G(RR)$  are dose rate dependent in the region  $10^{21} - 10^{23}$  ev/g hour.

In order that no dose rate dependence in the yields of A and RR be observed in the dose rate region  $10^{17} - 10^{22}$  ev/g hour, the radicals would either have to react exclusively by step IV.22 or exclusively by steps IV.23 and IV.24, over the whole dose rate range.

For reaction by step IV.22 only (i.e. pseudo first order, radical-substrate) to occur exclusively, the rate constant for reaction IV.22



would be given by  $k' > 10^3$  l/mole sec.

For reaction by only steps IV.23 and IV.24 to occur (i.e. second order radical-radical only), the rate constant for reaction IV.22 would be given by  $k' < 0.1$  l/mole sec.

(ii) Application to the Cyclohexene System

If the reactions in cyclohexene are free radical in nature, then species A and RR can be cyclohexane and dicyclohexyl respectively.

Reactions IV.22, IV.23 and IV.24 become reactions IV.16, IV.17 and IV.18 respectively. Since cyclohexyl radicals represent only a portion of the radicals present, the values of  $G(\text{cyclohexane})$  and  $G(\text{dicyclohexyl})$  will be less than the values of  $G(A)$  and  $G(RR)$  respectively, for  $G(\text{total radicals}) = 10$ . However, the general shape of the curves shown in Figure IV.2 for A and RR, will be essentially the same for the cyclohexene radiolytic products.

Figure IV.1 shows that there may have been a slight dose rate effect in the cyclohexene system in the lowest dose rate region covered. If this is a real effect then a value of  $k'_{IV.16} \approx 1$  l/mole sec is obtained for the cyclohexyl radical reaction IV.16, if radical-radical reactions are predominantly occurring over the dose rate region covered.



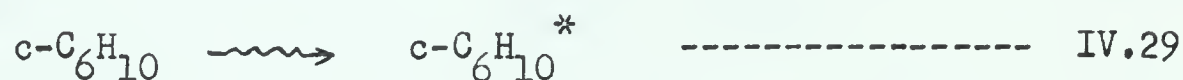


(B) MECHANISM FOR "PURE" LIQUID CYCLOHEXENE RADIOLYSIS

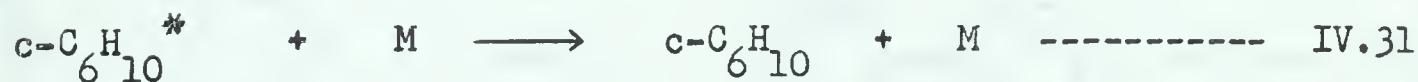
(a) The Mechanisms

Many mechanisms were tried that included radical-radical, radical-substrate, excited molecule, or ion-molecule reactions, or included combinations of these four reaction types. In almost all cases the mechanism failed to explain the experimental results. The most satisfactory mechanisms were the following

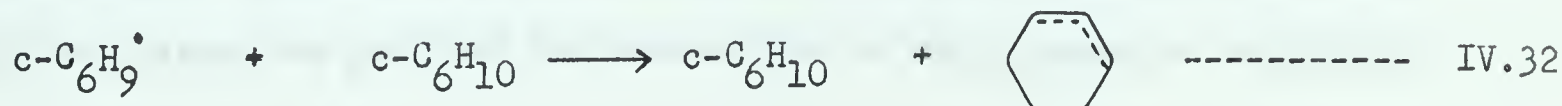
Mechanism (1)



where \* denotes an excited molecule.



where M is any collision partner causing deactivation of the excited cyclohexene molecule

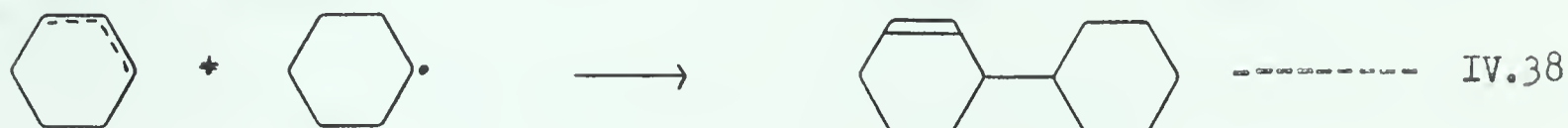






This step is included because it is now known whether or not C-H bond cleavage will occur specifically in the 3-position in step IV.30.

Reaction IV.32 is  $\sim 15 - 20$  kcal/mole exothermic. (69)



The disproportionation reaction between a cyclohexyl radical and a cyclohexenyl radical to yield cyclohexane and cyclohexadiene has been excluded, since the yield of cyclohexadiene in this system is negligible.

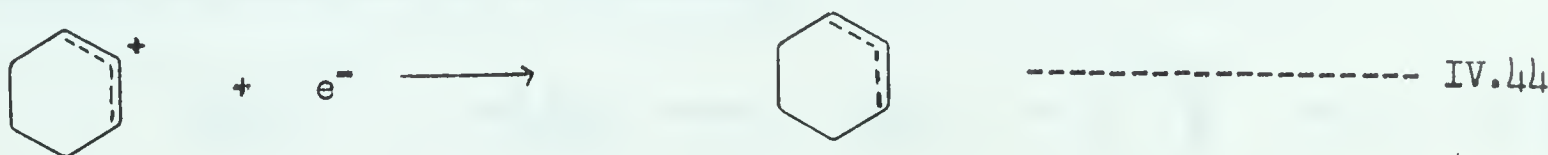
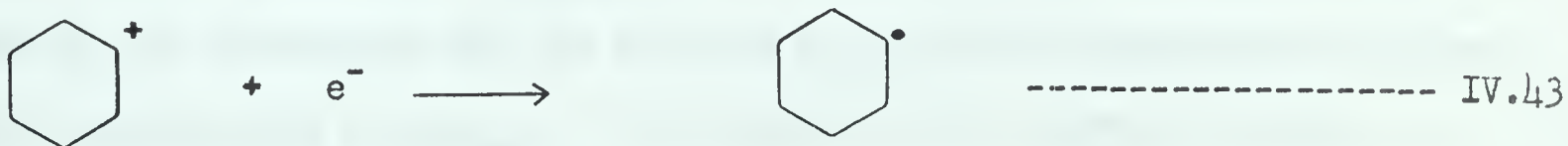
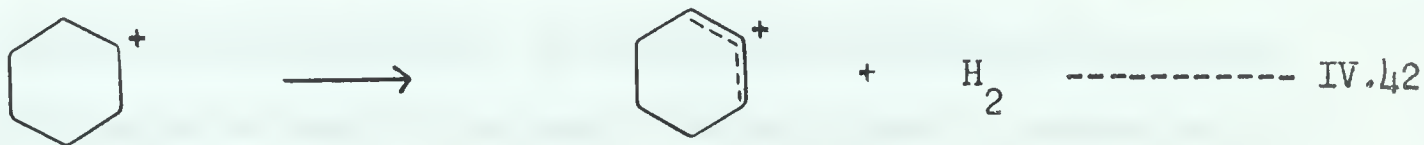
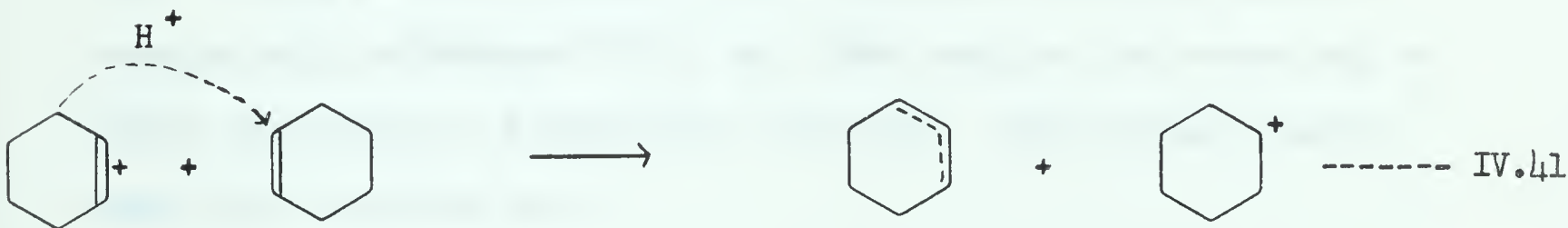
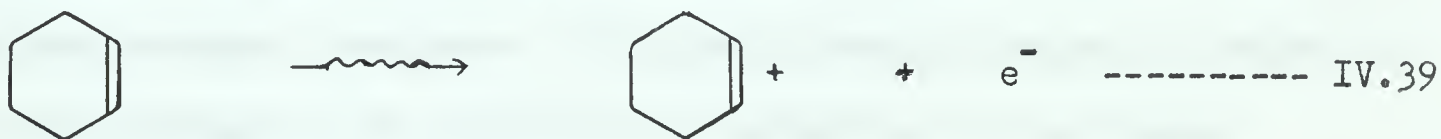
Because all of the cyclohexane yield apparently cannot be explained by step IV.36, there must be an alternative mode of formation for this



product. This will be discussed later.

Mechanism (2)

Reactions IV.29 - IV.34 of mechanism (1) cannot be distinguished from the following ionic reactions on the basis of the experimental evidence obtained in this work.





The radicals resulting from steps IV.41, IV.43 and IV.44 would react as in mechanism (1) by steps IV.35 - IV.38.

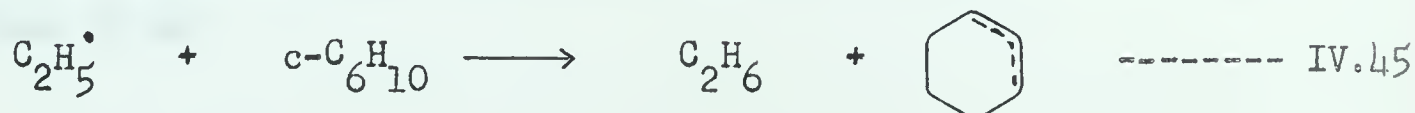
(b) Feasibility of the Mechanisms

(1) Fates of the Excited Molecules

Homolytic cleavage to yield a cyclohexenyl radical and an H-atom is the primary reaction considered. C-H bond cleavage appears to predominate over C-C bond cleavage in the liquid phase radiolysis of cyclohexene. Products arising from the latter were not exhaustively studied in this work.

Since the rate constant for an H-atom reacting with cyclohexene is  $\sim 10^9$  l/mole sec (36) (96) (cf.  $\sim 10^2$  l/mole sec for ethyl radicals reacting with cyclohexene (71) ), any other reaction for H-atoms may be safely neglected for  $\gamma$ -radiolysis conditions. Thus H-atoms react by steps IV.33 and IV.34 only.

The only reactions given for cyclohexyl radicals are the radical-radical reactions IV.35, IV.36 and IV.38. The calculation described in section IV. (A). (6) indicates that if cyclohexyl radicals react predominantly by radical-radical reactions,  $k_{IV.16} \approx 1$ . A value for this reaction was not found in the literature, but the value of  $k_{IV.16}$  will be expected to be less (36) than the value of  $k_{IV.45} = 230$  kcal/mole (71) reported for the corresponding reaction for ethyl radicals







No self-consistent mechanism could be found that included cyclohexyl radical attack on the substrate and also predicted the observed experimental results.

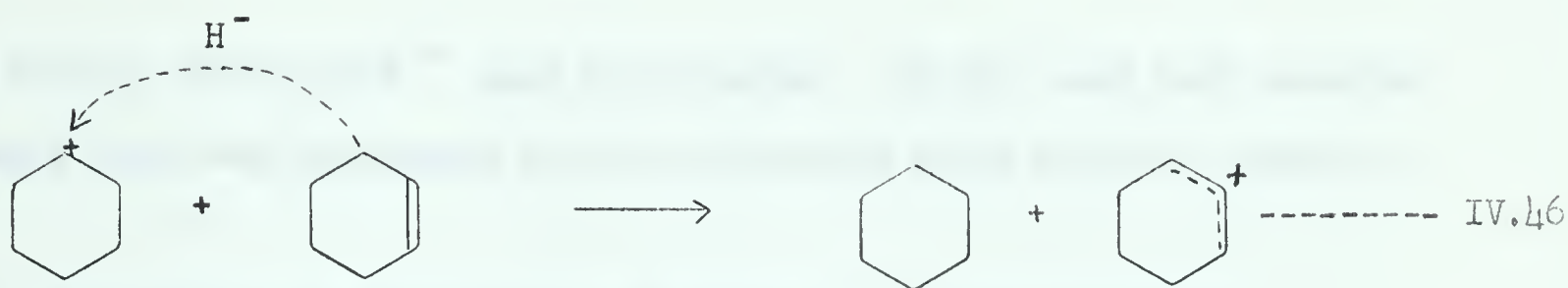
Due to resonance stabilization the average life time of the cyclohexenyl radicals will be larger than that of the cyclohexyl radicals. Thus if it is true that the cyclohexyl radicals react exclusively with other radicals, then it is certainly true for the cyclohexenyl radicals. No mechanism that included cyclohexenyl radical addition to substrate molecules could be found that also predicted the observed experimental results. Disproportionation reactions were omitted because of the negligible yield of cyclohexadiene. No information was found in the literature about such reactions for resonance stabilized radicals.

## (2) Fates of the Ionized Molecules

The ions formed in the initial radiation act may undergo chemical reactions, or they may be neutralized before enough time has elapsed for such reactions to take place.

The initial reaction suggested for an ionized cyclohexene molecule was proton transfer to another cyclohexene molecule (step IV.41). This type of reaction was suggested as being very probable by Collinson et al (67) in the liquid phase radiolysis of 1-hexadiene. The carbonium ion formed may undergo reactions IV.42 and IV.43 as suggested above. Alternatively hydride ion transfer from a cyclohexene molecule may occur, to form cyclohexane as given by reaction IV.46.





Hydride ion transfer has been reported for alkyl radical ions under mass spectrometric conditions (17).

Neutralization of the cyclohexenyl ion by step IV.44 would give a cyclohexenyl radical.

#### (c) A Note on Cyclohexane Formation

It has been pointed out that the cyclohexane is unlikely to be formed by cyclohexyl radical disproportionation reactions alone. Since the experimental results can apparently be fitted only to a mechanism in which the radicals (except H-atoms) react among themselves, a process forming cyclohexene must presumably be occurring that does not include cyclohexyl attack of a cyclohexene molecule. The net effect of steps IV.39, IV.41, and IV.46 above is the overall reaction IV.47 below



Such a mode of cyclohexane formation would fit the experimental results





as long as "free ions" \* were not involved. If free ions were involved then a dose rate dependence in the cyclohexane yield should be observed

(d) Agreement with Experimental Observations - Pure Cyclohexene  
and Cyclohexene-d<sub>10</sub>

The mechanisms outlined above in section IV (B) (a) predicts the observed dimeric products, dicyclohexyl, 3-cyclohexylcyclohexene, and 2,2'-dicyclohexenyl. Furthermore their yields are predicted in the observed order of magnitude, with the di-olefin having the highest yield and the saturated dimer.

The observed absence of a marked dose rate dependence in any of the products is satisfied by these mechanisms since no radical or ion is reacting in both a 1st and 2nd order reaction.

The observed effects on the product yields caused by replacing cyclohexene by cyclohexene-d<sub>10</sub> are consistent with these mechanisms. For mechanism (1) deuteration can be expected to increase the rate constant ratios  $k_{IV.31}/k_{IV.30}$ ,  $k_{IV.33}/k_{IV.34}$  and possibly  $k_{IV.35}/k_{IV.36}$ .

Ion-molecule reactions involving C-H bond cleavage may also be retarded by replacing the hydrogen by deuterium. Thus deuteration may increase the rate constant ratios  $k_{IV.40}/k_{IV.41}$  and  $k_{IV.43}/(k_{IV.42} + k_{IV.46})$ .

---

\* Free ions are pairs of ion that escape immediate recombination after they are generated in the liquid by irradiation.





Thus the observed decreases in the yields of hydrogen, cyclohexane and 2,2'-dicyclohexenyl, the observed increase in the yield of dicyclohexyl and also the slight increase in the yield of cyclohexylcyclohexene are all consistent with these mechanisms.



(C) THE EFFECT OF ADDITIVES ON THE CYCLOHEXENE RADIOLYTIC SYSTEM

(a) The Experimental Observations

The following experimental observations need to be explained.

(1) All "cyclohexene products" \* are inhibited by each of the three additives (i.e. by benzene, 1,3-cyclohexadiene and 1,4-cyclohexadiene), with the exception that cyclohexane formation is not inhibited by 1,4-cyclohexadiene. (Hydrogen suffered only slight inhibition in the 1,4-diene solution, but the effect was thought to be real).

(2) All of the "cyclohexene products" suffered their greatest inhibition when 1,3-cyclohexadiene was the additive.

(3) The relative rates of additive disappearance for any given concentration of additive were:-

1,3-cyclohexadiene > 1,4-cyclohexadiene > benzene

---

\* The term "cyclohexene products" refers to those products that were observed in the radiolysis of pure cyclohexene, i.e. hydrogen, cyclohexane, 2,2'-dicyclohexenyl, dicyclohexyl, 3-cyclohexylcyclohexene and D-1 . The polymer was not characterized and is not therefore included in this term.





(4) The percentage inhibition \* of hydrogen by each of the additives in cyclohexene-d<sub>10</sub> was similar to the percentage inhibition caused by that additive in cyclohexene.

(5) Cyclohexane experienced >80% inhibition in a 10% solutions of 1,3-cyclohexadiene in cyclohexene, but suffered no inhibition, and possibly slight enhancement, when 1,4-cyclohexadiene was the additive.

(6) When 1,3-cyclohexadiene was added to cyclohexene, a dimer of 1,3-cyclohexadiene (i.e. dicyclohexadiene) was formed in good yield ( $G \approx 6$ ), even at low diene concentration ( $\epsilon_{1,3\text{-diene}} \approx 0.02$ ). The yield of this product reached a maximum of  $G = 6.3$  at  $\epsilon_{1,3\text{-diene}} \approx 0.05$ , and then decreased with increasing 1,3-cyclohexadiene concentration. This dimer was also formed when a dilute solution of 1,3-cyclohexadiene ( $\epsilon_{1,3\text{-diene}} = 0.006$ ) in cyclohexane was irradiated.

(7) Although dimeric products arising from the reaction of dicyclohexadienyl radicals were apparently observed when solutions of 1,4-cyclohexadiene in cyclohexene were irradiated, no such products were observable when 1,3-cyclohexadiene was the additive.

\* For any "cyclohexene product" the percentage inhibition

$$= 100 \left( \frac{G_{\text{ex}} - G_{\text{obs}}}{G_{\text{ex}} - G_a^0} \right) \quad \text{where}$$

$G_{\text{ex}}$  is the expected yield of the product (see page 111 for the definition),  $G_{\text{obs}}$  is the observed yield and  $G_a^0$  is the yield of the product from the pure additive.



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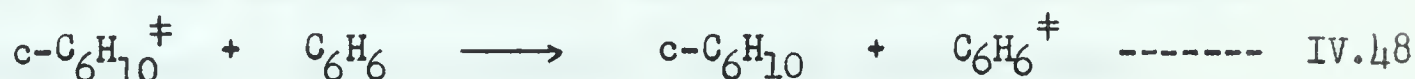
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(8) The rate of consumption of 1,3-cyclohexadiene was higher when the diene was added to cyclohexene-d<sub>10</sub> than when it was added to cyclohexene. (The yield of dicyclohexadiene may also have been higher, but the measurement was not very reliable since the yield of this dimer is extremely sensitive to small changes in the concentration of 1,3-cyclohexadiene for  $\epsilon_{1,3\text{-diene}} < 0.02$ ).

(9) Only 1,3-cyclohexadiene solutions gave high polymer yields.

(b) Effect of Benzene Addition

There appears little doubt that "sponge type" (45) protection by benzene occurs in liquid radiolytic systems such as cyclohexane (53) (79). It was observed in this work that all of the "cyclohexene products" were inhibited by benzene. The relative degrees of inhibition for each of the major products were consistent with a general activation transfer reaction given by



It was not possible to draw meaningful conclusions about the nature of the activated  $c\text{-C}_6\text{H}_{10}^{\ddagger}$  species, on the basis of the data obtained. Thus  $c\text{-C}_6\text{H}_{10}$  may have been changed and/or excited. The yields of products that might have resulted from a radical scavenging process appeared to be low ( $G < 0.1$ ). Thus it appears that sponge type protection by benzene occurred in the cyclohexene system, benzene acting as an energy trap. Since benzene



is relatively more stable than the other hydrocarbons studied most of the activation energy would eventually be dissipated through the system by collisional processes.

Benzene has a higher ionization potential than 1,3-cyclohexadiene<sup>\*</sup>. Thus inhibition of the "cyclohexene products" by charge transfer from ionized cyclohexene molecules to solute molecules may be a more probable process when the additive is 1,3-cyclohexadiene, than when it is benzene. This may explain why 1,3-cyclohexadiene inhibits the "cyclohexene products" more effectively than does benzene.

---

\* The appearance potential for benzene obtained by electron impact study in this work was  $9.9 \pm 0.3$  ev (see Table III.31). This was higher than the value of  $9.52 \pm 0.08$  ev (97) obtained by Morrison using a similar method. Both of these values were higher than a spectroscopic value of 9.24 ev (98), reported for the formation of (benzene)<sup>+</sup>. Thus the reliability of the value obtained for benzene by electron impact is open to question. For the series butane, 2-butene and butadiene, spectroscopic values for the first ionization potentials were reported as 10.34, 9.24 and 9.07 ev, respectively (98). The spectroscopic value of the energy for (cyclohexene)<sup>+</sup> formation was reported as  $9.2 \pm 0.05$  (99) so is similar to 2-butene. It therefore appears reasonable to accept the values obtained for the appearance potentials obtained in this work insofar as they show (cyclohexene)<sup>+</sup>,

(Continued on next page)

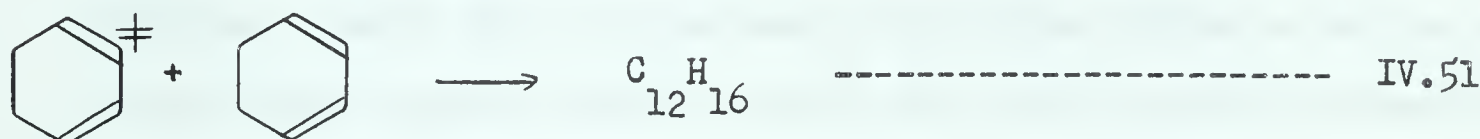
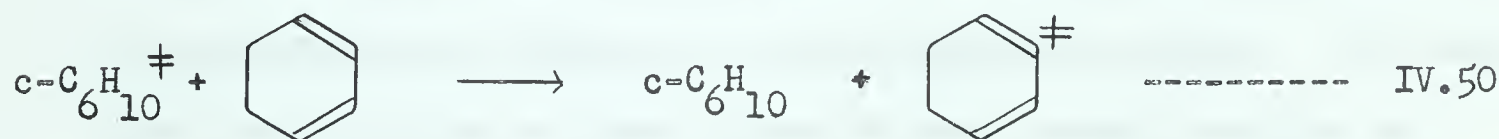




(c) Effect of 1,3-cyclohexadiene Addition

The G-value of the 1,3-cyclohexadiene dimer, dicyclohexadiene, increased very sharply from zero to a value of  $\approx 6$  as the electron fraction of 1,3-cyclohexadiene was increased from zero to  $\sim 0.02$  (Figures III.10 and III.12). The yield of this dimer reached a maximum value of 6.3 at  $\phi_{1,3\text{-diene}} \approx 0.05$ .

The high yield of a product arising solely from the solute in this low concentration region clearly indicates excitation and/or charge transfer from the activated solvent (cyclohexene) to the 1,3-cyclohexadiene, as shown by equations IV.49, IV.50 and IV.51.



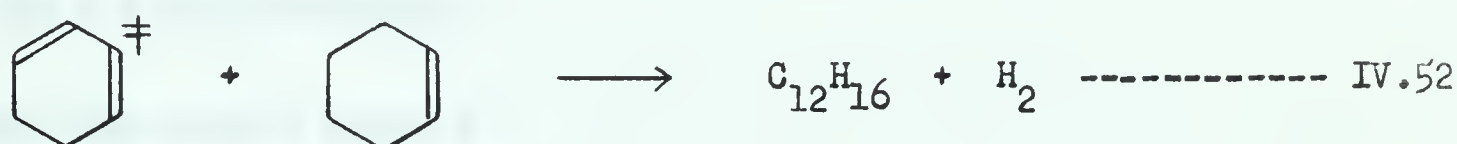
where  $\neq$  denotes either a charged or an excited molecule.

$(\text{cyclohexene-d}_{10})^+$  and  $(1,4\text{-cyclohexadiene})^+$  having the same value of  $9.2 \pm 0.2$  ev and 1,3-cyclohexadiene having a lower value of  $8.7 \pm 0.3$  ev.





The fact that a  $C_{12}H_{16}$  species was also formed when a dilute solution of 1,3-cyclohexadiene in cyclohexane was irradiated indicates that reaction IV.52, involving a cyclohexene molecule, probably did not occur.



Strengthening this conclusion was the reported formation of a dimer of 2,3-dimethyl-1,3-butadiene when a dilute solution of this di-olefin in cyclohexanone was irradiated (100).

Although the yields of the individual "cyclohexene type" dimers could not be measured for solutions where  $\{_{1,3\text{-diene}} > 0.002$ , it is clear that they were decreasing extremely rapidly with increasing 1,3-cyclohexadiene addition in this concentration region. The fact that the inhibition of these dimers is more marked than that of hydrogen suggests that the decrease in the dimer yields is due not only to the energy transfer reaction IV.50, but also to radical scavenging. It has been reported that methyl radicals add  $\sim 700$  times more readily to 1,3-cyclohexadiene than to cyclohexene (34). A similar difference in addition rate may be expected for  $C_6$ -hydrocarbon radicals. Such a radical scavenging mechanism can lead to polymer formation as described below.

Of the  $C_6$ -ring olefins studied in this work only 1,3-cyclohexadiene can form a long chain polymer with the repeating  $C_6$ -rings unopened. In



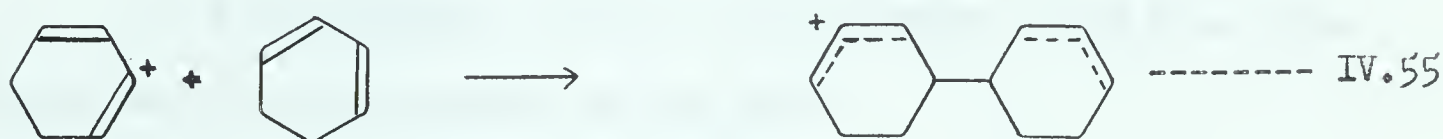
the cases of cyclohexene and 1,4-cyclohexadiene, formation of a trimer is sterically hindered and formation of a tetramer by successive monomer addition is impossible without some ring cleavage. Both ionic and free radical polymerization appears possible for 1,3-cyclohexadiene.

The free radical path is



etc.

The first step in the ionic polymerization can be



The radical-ion formed in step IV.55 can add a monomer unit to either ring. Alternatively ring closure can yield the dimer, dicyclohexadiene. The dimerization should be favoured at low concentrations of 1,3-cyclohexadiene while polymerization by both mechanisms should be favoured by increasing the concentration of the diene. This agrees with the observation that the yield of dicyclohexadiene decreased as  $\left( \begin{smallmatrix} \text{1,3-diene} \end{smallmatrix} \right)$  is increased above  $\sim 0.05$ ,





while  $G(\text{polymer})$  increased rapidly with increasing 1,3-cyclohexadiene content (see Figure III.14).

The cyclohexane yield was markedly reduced by the addition of a low concentration of 1,3-cyclohexadiene. Either charge or energy transfer or radical scavenging could account for this. At  $\epsilon_{1,3\text{-diene}} \approx 0.10$  the yield of cyclohexane was  $G \approx 0.15$ . This part of the cyclohexane yield was apparently not inhibitable since the yield of cyclohexane for solutions where  $\epsilon_{1,3\text{-diene}} > 0.10$  was apparently proportional to  $\epsilon_{\text{cyclohexene}}$ . The hydrogen yield was inhibited less than the yields of the other "cyclohexene products" by the addition of 1,3-cyclohexadiene. This appears to indicate that not all of the observed reactions in the cyclohexene system could arise from ionic species, since in such an event the added 1,3-cyclohexadiene would be expected to inhibit all of the cyclohexene products to the same degree.

If a considerable portion of the hydrogen yield arose from H-atom abstraction reactions of the type



then the yield would be less affected than the yields of the other "cyclohexene products" by the addition of the 1,3-cyclohexadiene. This is because the difference in the rate of H-atom reaction with cyclohexene and with 1,3-cyclohexadiene is not as great as the difference for a





larger radical reacting with these compounds.\* Thus it appears that at least some of the hydrogen yield arises from H-atom reactions.

The energy transfer reaction IV.50 is in competition with reaction IV.57 below



Since several C-H bond cleavage processes are involved in IV.57 the ratio  $k_{\text{IV.50}}/k_{\text{IV.57}}$  will be expected to increase if cyclohexene is replaced by cyclohexene-d<sub>10</sub> in the system. This may explain why the rate of consumption of 1,3-cyclohexadiene is higher when the diene is added to cyclohexene-d<sub>10</sub> than when it is added to cyclohexene.

(d) Effect of 1,4-Cyclohexadiene Addition

As  $\epsilon_{1,4\text{-diene}}$  was increased from zero to 0.10 there was a marked increase in the yield of two types of dimer, D-2 and D-3, that had not been formed in irradiated cyclohexene.

---

\* The respective rates of methyl radical addition to and abstraction from 1,3-cyclohexadiene are ~700 and ~350 times faster than the respective rates of addition to and abstraction from cyclohexene (34). The rate for H-atom addition to butadiene is only 10 times faster than the addition to cis2-butene (101).



These were tentatively identified as cyclohexenylcyclohexadiene (D-2) and dicyclohexadienyl (D-3) on the basis of their retention times on the silica-gel and silicone rubber V.P.C. columns. Although these products were not positively identified, it did appear that their formation involved cyclohexadienyl radical precursors. No direct dimerization product was observed that corresponded to the dicyclohexadiene formed in the 1,3-cyclohexadiene solution. Added evidence for the presence of cyclohexadienyl radicals in the 1,4-cyclohexadiene/cyclohexene solutions was the formation of 1,3-cyclohexadiene as a product, and the fact the yield of this product had a dependence on the value of  $\epsilon_{1,4\text{-diene}}$  that was similar to the dependence shown by D-2 and D-3 (see Figure III.11). Also, cyclohexadienyl radicals have been detected in irradiated 1,4-cyclohexadiene (31).

The radicals can arise at low 1,4-cyclohexadiene concentration in the observed yield (i) from the decomposition of 1,4-cyclohexadiene, following energy transfer from the cyclohexene or (ii) by a metathetical reaction between radicals of the cyclohexene system and 1,4-cyclohexadiene. Neither of these processes alone can fit the experimental data, but if both processes occurred a fit may be obtained.

It was concluded for the cyclohexene system that the radicals reacted only among themselves. For such a condition it was calculated that the rate constant for hydrogen abstraction from a cyclohexene molecule would be  $k \lesssim 1 \text{ l/mole sec}$ . The abstraction of an H-atom from 1,4-cyclohexadiene can be expected to be easier than from cyclohexene (89).



There are several things to be considered in this connection. First, the fact that the system is not a simple one, but a complex one, is a fact which must be taken into account. Second, the fact that the system is not a static one, but a dynamic one, is a fact which must be taken into account. Third, the fact that the system is not a homogeneous one, but a heterogeneous one, is a fact which must be taken into account. Fourth, the fact that the system is not a uniform one, but a non-uniform one, is a fact which must be taken into account. Fifth, the fact that the system is not a continuous one, but a discontinuous one, is a fact which must be taken into account. Sixth, the fact that the system is not a perfect one, but an imperfect one, is a fact which must be taken into account. Seventh, the fact that the system is not a complete one, but an incomplete one, is a fact which must be taken into account. Eighth, the fact that the system is not a self-contained one, but a dependent one, is a fact which must be taken into account. Ninth, the fact that the system is not a self-sufficient one, but a non-self-sufficient one, is a fact which must be taken into account. Tenth, the fact that the system is not a self-reliant one, but a non-self-reliant one, is a fact which must be taken into account. Eleventh, the fact that the system is not a self-sustaining one, but a non-self-sustaining one, is a fact which must be taken into account. Twelfth, the fact that the system is not a self-perpetuating one, but a non-self-perpetuating one, is a fact which must be taken into account. Thirteenth, the fact that the system is not a self-renewing one, but a non-self-renewing one, is a fact which must be taken into account. Fourteenth, the fact that the system is not a self-regulating one, but a non-self-regulating one, is a fact which must be taken into account. Fifteenth, the fact that the system is not a self-organizing one, but a non-self-organizing one, is a fact which must be taken into account. Sixteenth, the fact that the system is not a self-maintaining one, but a non-self-maintaining one, is a fact which must be taken into account. Seventeenth, the fact that the system is not a self-protecting one, but a non-self-protecting one, is a fact which must be taken into account. Eighteenth, the fact that the system is not a self-defending one, but a non-self-defending one, is a fact which must be taken into account. Nineteenth, the fact that the system is not a self-asserting one, but a non-self-asserting one, is a fact which must be taken into account. Twentieth, the fact that the system is not a self-fulfilling one, but a non-self-fulfilling one, is a fact which must be taken into account.

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If in the former case the rate constant were  $k \approx 10$  l/mole sec then reaction IV.58 would be possible



This reaction would predict a rise in the yield of cyclohexane. However, since the reaction corresponding to IV.58 that involves cyclohexenyl radicals is  $\sim 15 - 20$  kcal less exothermic than reaction IV.58, it follows that the yield of dicyclohexyl should be markedly inhibited while that of 2,2'-dicyclohexenyl should hardly be inhibited at all. This is not the observed experimental result. Both 2,2'-dicyclohexenyl and dicyclohexyl are inhibited, although the effect in the latter case is slightly greater.

If energy transfer to the 1,4-cyclohexadiene, followed by homolytic cleavage of the diene to yield an H-atom and the cyclohexadienyl radical was the only source of these radicals then it would be expected that the yield of cyclohexane would be inhibited. In fact it appeared to be slightly enhanced, which indicates that the radical process for cyclohexadienyl formation is also occurring.

Since both cyclohexene and cyclohexadiene have similar hydrogen yields, inhibition effects are not observable on the basis of the total yield. If energy transfer from the cyclohexene to the 1,4-cyclohexadiene



Let  $\mathcal{C}$  be the category of  $\mathbb{C}$ -modules and  $\mathcal{D}$  the category of  $\mathbb{R}$ -modules.

Consider the functors  $F: \mathcal{C} \rightarrow \mathcal{D}$  and  $G: \mathcal{D} \rightarrow \mathcal{C}$  defined by

$$F(M) = M \otimes_{\mathbb{C}} \mathbb{R} \quad \text{and} \quad G(N) = N \otimes_{\mathbb{R}} \mathbb{C}.$$

The functor  $F$  is called the forgetful functor and  $G$  is called the complexification functor.

Verify that  $F$  and  $G$  are adjoint functors, i.e.  $\text{Hom}_{\mathcal{D}}(F(M), N) \cong \text{Hom}_{\mathcal{C}}(M, G(N))$ .

Moreover, verify that  $F$  and  $G$  are both faithful and full functors.

Is  $F$  an equivalence of categories? Justify your answer.

Is  $G$  an equivalence of categories? Justify your answer.

What is the image of  $F$  in  $\mathcal{D}$ ? What is the image of  $G$  in  $\mathcal{C}$ ?

Describe the kernel of  $F$  and the kernel of  $G$ .

What is the relationship between  $F$  and  $G$  on the level of objects?

Let  $M$  be a  $\mathbb{C}$ -module. What is  $F(M)$  as an  $\mathbb{R}$ -module?

Let  $N$  be an  $\mathbb{R}$ -module. What is  $G(N)$  as a  $\mathbb{C}$ -module?

Let  $M$  be a  $\mathbb{C}$ -module. What is  $F(M)$  as a  $\mathbb{C}$ -module?

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Let  $M$  be a  $\mathbb{C}$ -module. What is  $F(M)$  as a  $\mathbb{C}$ -module?

were highly efficient, then even for a 10% solution of 1,4-cyclohexadiene the hydrogen produced in cyclohexene-d<sub>10</sub> might be expected to be almost all H<sub>2</sub> and HD. This is not the case, as can be seen from Table III.25.



(D) SUMMARY OF CONCLUSIONS

It seems clear from the nature and distribution of the products from irradiated cyclohexene and cyclohexene-d<sub>10</sub>, that radicals play an important role in this system. However it is not clear to what extent the precursors of the radicals are ionic species and to what extent they are excited molecules. The most satisfactory explanation for the absence of a dose rate dependence in the cyclohexene product yields appears to be that the cyclohexyl and cyclohexenyl radicals react among themselves, and do not react to an appreciable extent with the substrate in the dose rate region studied.

The benzene inhibition of cyclohexene radiolysis is consistent with a "sponge type" protection mechanism.

When 1,3-cyclohexadiene was added to cyclohexene it is clear from the high yield of dicyclohexadiene and the nature of the dependence of this yield on  $\epsilon_{1,3\text{-diene}}$ , that activation transfer (energy or charge) from substrate to 1,3-cyclohexadiene was a major process. Chain polymerization was also an important feature.

The inhibition of the dimeric products from cyclohexene, while the cyclohexane yield was slightly enhanced, could not be explained on the basis of a single process. If some energy transfer from the cyclohexene to the added 1,4-cyclohexadiene occurred, and at the same time cyclohexyl radicals reacted with the diene to yield cyclohexadienyl radicals by a metathetical process, then a fit between the experimental



results and the mechanism could be obtained.



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CHARLES THE FIRST

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CHAPTER II

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